Atmospheric deposition of TiO_2 films on glass substrates for anti-bacterial activity

Zulfiqur Ali*, Ross Gimblett, David Lax and David Meakins

School of Science and Technology, University of Teesside,
Middlesbrough, United Kingdom, TS1 3BA

ABSTRACT

A process based on a simulation of an industrial float line has been used for deposition of TiO_2 on glass slides. The process is operated at atmospheric pressure rather than under vacuum condition. A variety of organic pre-cursors can be used for TiO_2 formation and films of varying thickness can be produced. Illumination of the TiO_2 coated slides with UVc light had significant anti-microbial effects on *Ps.aeruginosa* cells in suspension.

Keywords: TiO_2, atmospheric chemical vapour deposition, anti-bacterial

1. INTRODUCTION

TiO_2 acts as a photocatalyst for the air-oxidation of organic compounds. Its aqueous suspensions, powders and supported coatings have been applied in the oxidative stripping of organic compounds from air and water[1-5]. TiO_2 films have also be studied for photocatalytically self-cleaning windows[6]. The application of titanium dioxide thin films prepared by the sol-gel method for the photocatalytic sterilization of microbial cells has recently been reported[7]. Goswami *et. al.* have demonstrated the anti-bacterial effect of photocatalytic oxidation in indoor air using titanium dioxide catalyst[8]. Several reports have demonstrated the application of slurried titanium dioxide particles for water disinfection[9,10]. In the scale-up development of photocatalytic processes filtration and resuspension are to be avoided, this can be realised by fixing the catalyst onto a support. Butterfield *et. al.* have developed a water disinfection system using an immobilised titanium dioxide film in a photochemical reactor[11]. The photocatalytic properties of titanium dioxide films can be maintained on a wide range of substrates including polymers[12].

Titanium dioxide has a bandgap energy of 3.0-3.3eV. Illumination of light of wavelength 376-413nm can promote an electron from the valence band to the conduction band creating a deficiency (hole) in the valence band. When these charges migrate to the surface then the reaction of a photogenerated electron with a reducible absorbed species and/or hole with an oxidable adsorbed species can occur[13,14]. Interaction with water and oxygen leads to the formation of radicals which are thought to be the primary bactericidal agents[15,16].

$$h^+ + H_2O \rightarrow .OH + H^+$$

$$e^- + O_2 + H^+ \rightarrow .OOH$$

Currently used sol-gel methods for titanium dioxide film deposition lead to organic contaminants remaining within the films. Atmospheric chemical vapour deposition (CVD) methods are well documented in the literature and have been shown to lead to extremely durable metal oxide films on a variety of substrates[17]. We have designed and built an atmospheric CVD furnace, which simulates the float line glass process and produces high optical quality and durable metal oxide films on a variety of flat substrates including polymers. The atmospheric CVD furnace can be modified to allow coating on different substrate configuration including cylinders and spheres.

* Correspondence: Email: z.ali@tees.ac.uk

2. EXPERIMENTAL

2.1 FILM DEPOSITION

Glass slides were coated with TiO_2 by vapourising the organic liquid pre-cusor tetra-iso-propyltitanate (TIPT). The float line simulator gives sufficient vapour density to produce varying thicknesses of TiO_2. The glass substrate is placed in a slot in a movable carriage. The substrate is heated using resistive heaters; the heaters are heated at a rate of 10 $^{o}C.min^{-1}$ until the desired temperature is obtained. The depositing chamber is heated at a rate of 25 $^{o}C.min^{-1}$ using radiative heaters. The vaporising trough containing the liquid organic precusor is heated using a heating element, to the required temperature. A small flow of nitrogen is maintained in the trough to keep the precursor in a nitrogen atmosphere; this avoids self-ignition of the vapour. The nitrogen is bubbled through a copper pipe, in the vapourising trough, which has fourteen 1.5mm holes drilled equally spaced along its 170mm length. The glass substrate and the vaporising trough are maintained for ten minutes at the appropriate temperature to achieve equilibrium. The carriage containing the glass substrate is moved along the depositing chamber at a set speed. The nitrogen flow rate in the vaporising trough is increased; this forces the vapour through the depositing chamber and into an extraction system. The film thickness, quality and uniformity was influenced by substrate temperature together with both transport speed and the rate of gas flow across the substrate. The conditions employed to produce various thicknesses of films is given in table 1. The film thickness is directly related to the reflective colour from the substrate; the colour of films ranged from silver, having thickness of approximately 25nm, to green films having thickness of approximately 115nm. The film thickness was measured using a tallysurf; in this instrument a fine needle traverses across from substrate to coating. The plots for various thicknesses of films are shown in figure 1.

	Silver	Gold	Red	Blue	Green
Substrate temp. (^{o}C)	400	450	450	450	450
Depositing chamber temp. (^{o}C)	250	250	200	100	100
Vaporising trough temp. (^{o}C)	100	100	110	120	125
Nitrogen flow (dm^3min^{-1})	25	30	10	10	10
Coating speed ($x10^{-3}$ ms^{-1})	20	12	6	5.5	5.5

Table 1 Operating conditions for TiO_2 films using TIPT pre-cursor

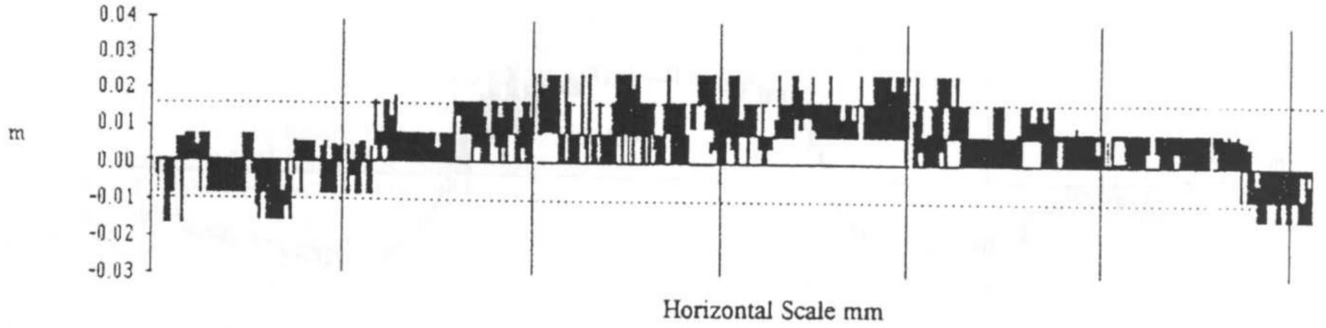
2.2 ANTI-MICROBIAL ACTIVITY

The anti-microbial properties of the glass-immobilised TiO_2 after photoactivation with UVc light was investigated using the ocular pathogen *Ps.aeruginosa*. TiO_2-coated glass slides (x3) were washed in PBS buffer. The slides were transferred to a clean polystyrene petri dishes containing $25cm^3$ PBS. The PBS was removed from the petri dishes and $25cm^3$ of bacterial suspension was added. The TiO_2-coated glass slides were exposed along with three control glass slides to UVc light.

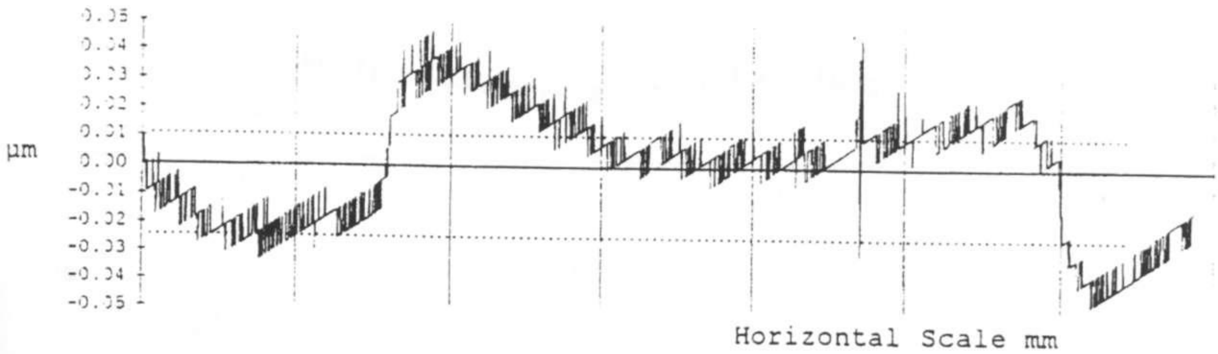
3. RESULTS AND DISCUSSION

The thickness profile measurements of the various coloured films, using the tallysurf are shown in figures 1a and 1b. It shows that a variety of film thicknesses can be produced. In this study, glass slides were used. Coating of larger areas would need more careful control of the substrate temperatures since non-uniformity of temperature across the substrate would lead to non-uniform films.

Silver Coating Colour
approximately 25nm thick



Gold Coating Colour
approximately 35nm thick



Red Coating Colour
approximately 85nm thick

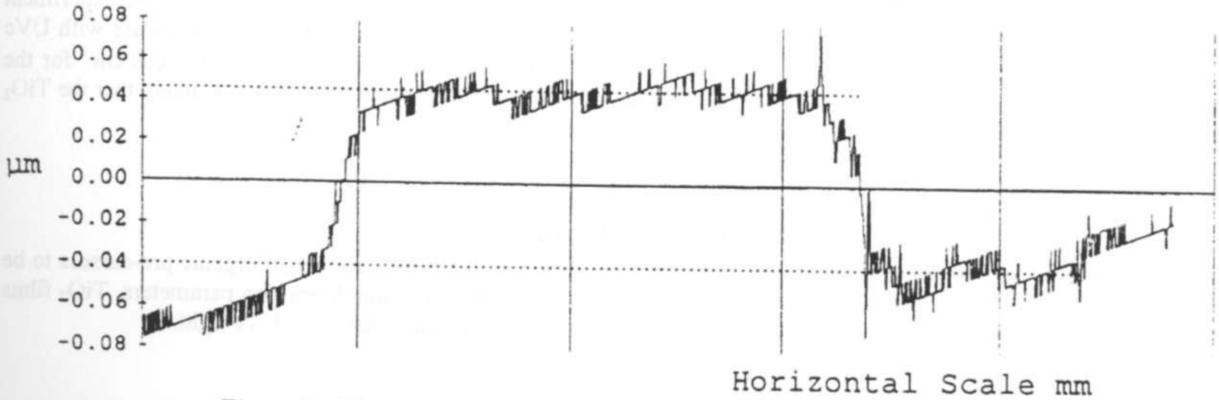


Figure 1a. Film thickness plots for TIPT films having silver to red colour

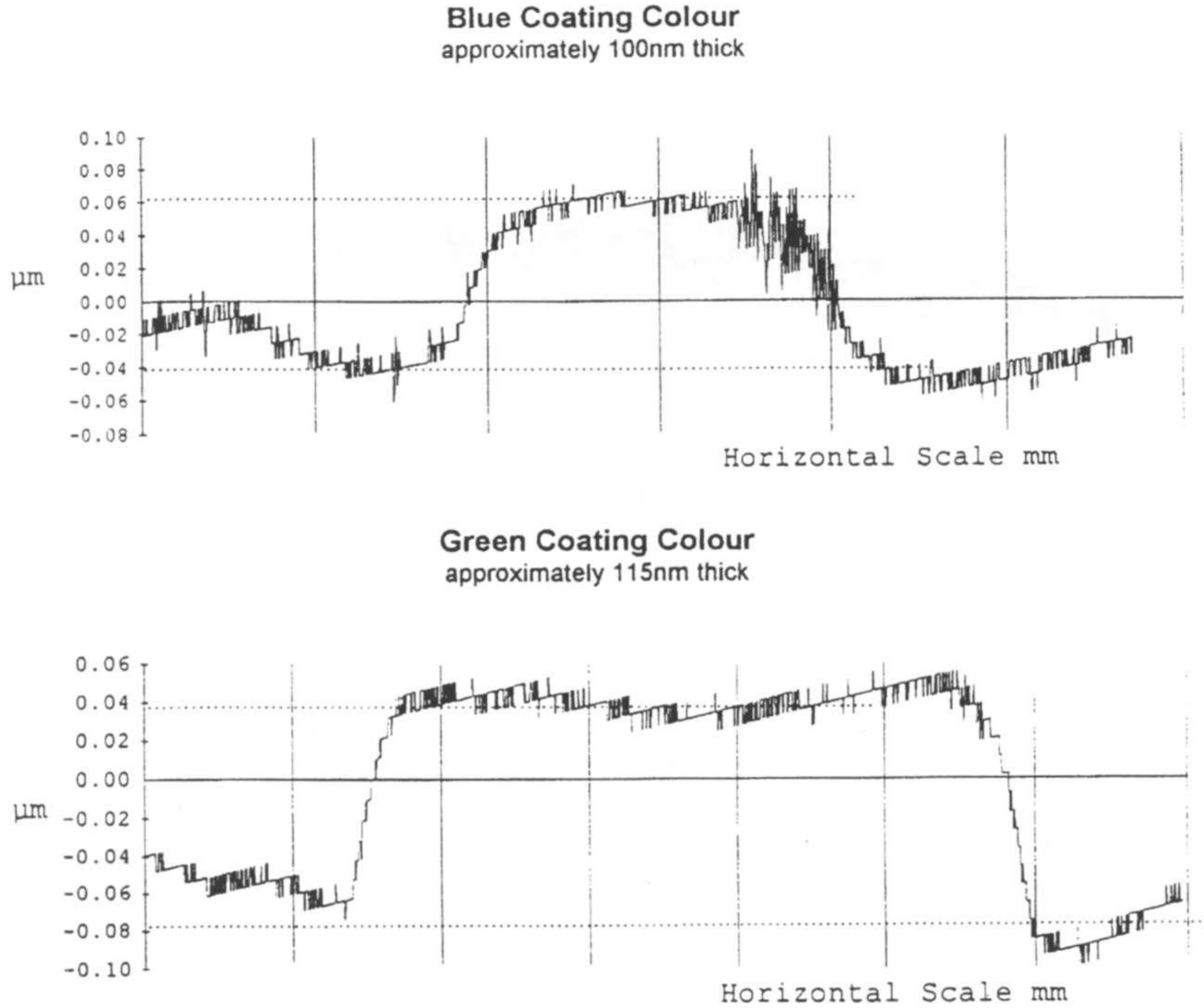


Figure 1b. Film thickness plots for blue and green colouredTIPT films

The anti-microbial properties of the TiO_2-coated glass after photoactivation were investigated by exposing the glass substrate to *Ps.aeruginosa*. There was a reduction in the viability of the *Ps.aeruginosa* suspension during the 3 hours of the experiment from $1x10^7$ to $2x10^6$ cells.cm^{-3}. Exposure of the *Ps.aeruginosa* solution to a glass control and TiO_2 coated glass with UVc light showed a decrease in cell number of $2x10^5 \pm 1.5x10^4$ cells.cm^{-3} for the former and $4.5x10^4 \pm 2x10^4$ cells.cm^{-3} for the latter. It is, therefore, clear that the TiO_2-coated glass shows enhanced anti-microbial properties. It is also likely that the TiO_2 coating will reduce the adhesion of the bacteria onto the slides.

4. CONCLUSION

An atmospheric chemical vapour deposition systems has been developed which allows a variety of organic pre-cursors to be employed in the formation of TiO_2 films. The film thickness can be controlled by altering deposition parameters. TiO_2 films produced from TIPT monomer were shown to have anti-bacterial properties under illumination of UVc light.

5. ACKNOWLEDGEMENTS

This work was partially supported by Tioxide Specialities Ltd.

6. REFERENCES

1. R.W. Matthews and S.R. McEvoy, *J. Photochem. Photobiol. A:Chem.*, 64, 231, 1992
2. T. Sakata and T. Kawai, *Chem. Phys.*, 80, 341, 1981
3. J. Peral and D. Ollis, *J. Catalysis*, 136, 554, 1992
4. L.A. Dibble and G.B. Raupp, *Catalysis Lett.*, 4, 345, 1990
5. W.A. Zeitner, C.G. Hill and M.A. Anderson, *Chemtech*, 21, May 1993
6. Y. Paz, L. Rabenberg and A. Heller, *J. Mater. Res.*, 10(11), 2482, 1995
7. Y. Horie, M. Tanya, and S. Tone, *Kagaku Kogaku Ronbunshu*, , 22(5), 1241, 1996
8. D.Y Goswami,., D.M. Trivedi, and S.S. Block, *J. Solar Energy Eng. Trans. ASME*, , 119(1), 92, 1997.
9. Y. Horie, M. Tanya, D.A. David, and S. Tone, *Indus. and Eng. Chem. Research*, 35(11), 3920, 1996
10. X.Z. Li, M. Zhang, and H. Chua, *Water Science and Technology*, 33(3), 111, 1996
11. I.M. Butterfield, P.A. Christensen, T.P. Curtis, and J. Gunlazuardi, *J. Water Research*, 31(3), 675, 1997
12. E. Bargarello, N. Serpone, P. Liska, W. Erbs, M. Gratzel, and E. Pelizzetti, E., *Gazz. Chim. Ital.*, 115, 599, 1985
13. N. Serpone, and E. Pelizzetti, eds., *'Photocatalysis'*, Wiley, New York, 1989
14. A.J. Bard, *J. Phys. Chem.*, 86, 172, 1982
15. H.N. Pham, H.N., T. McDowell, E. Wilkins, *J. Environ., Sci., Health*, 1995, A30(3), 627-636.
16. M. Stevenson, K. Bullock, W.Y. Lin, and K. Rajeshwar, *Research on Chemical Intermediates*, , 23(4), 311, 1997
17. D. Lax, and A.M. Sohi, *Rivistra della Staz - Sper Vetro*, 6, 163, 1986