Thin Solid Films 571 (2014) 75–83

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

The effect of process parameters on the structure, photocatalytic and self-cleaning properties of TiO_2 and Ag-TiO_2 coatings deposited using reactive magnetron sputtering

P. Navabpour [a,*], S. Ostovarpour [b], J. Hampshire [a], P. Kelly [b], J. Verran [b], K. Cooke [a]

[a] Teer Coatings Ltd, Miba Coating Group, West Stone House, Berry Hill Industrial Estate, Droitwich WR9 9AS, UK
[b] Manchester Metropolitan University, Faculty of Science and Engineering, Chester Street, Manchester M1 5GD, UK

ARTICLE INFO

Article history:
Received 12 November 2013
Received in revised form 7 October 2014
Accepted 7 October 2014
Available online 16 October 2014

Keywords:
Reactive magnetron sputtering
Silver
Titanium dioxide
Photocatalysis
Antimicrobial property

ABSTRACT

This article reports on the morphology, structure, wettability, photocatalytic and mechanical properties of TiO_2 and Ag-TiO_2 thin films, with the latter also displaying antimicrobial activity. The coatings were deposited using reactive closed field unbalanced magnetron sputtering. It was possible, by varying the process parameters, to tailor the structure and composition of the coatings. TiO_2 coatings which were deposited from a single titanium target (thickness ~1 μm) were relatively dense with low crystallinity and a mixed anatase and rutile structure. The addition of silver resulted in the formation of submicron sized silver particles dispersed throughout the coating. TiO_2 coatings deposited from two titanium targets (thickness ~2 μm) had a mixed anatase and rutile structure with a less dense topography. Ag-TiO_2 coatings deposited using this process showed a uniform dispersion of silver throughout the coating. All coatings presented excellent adhesion to the substrate and high photocatalytic activity under fluorescent light. Annealing at 600 °C had a detrimental effect on the photocatalytic activity as well as the mechanical properties of the coatings. The coatings deposited from a single Ti target were evaluated for their antimicrobial potential against *E. coli*. No reduction in the number of bacteria was observed using TiO_2. Ag-TiO_2 coatings, however, showed antimicrobial properties in the dark as well as light conditions, as a result of the innate antimicrobial potential of silver.

1. Introduction

Titanium dioxide is a widely studied semiconductor. It can be found in anatase, rutile and brookite crystal structures, with a band gap ranging between 3.0 for the rutile and 3.2 for the anatase structures [1]. Two main properties result from the presence of the TiO_2 band gap: photoelectrochemical energy conversion (as a semiconductor) and photocatalytic function [2]. The photoelectrochemical properties open up applications for this semiconductor in photovoltaics. On the other hand, its photocatalytic properties mean that TiO_2 can catalyse the degradation of pollutants and microbial organisms, making it attractive where there is a demand for hygiene and cleanliness. The applications include food and beverage process surfaces as well as medical devices and surfaces [3,4].

Several studies have been carried out to investigate the effect of crystal structure of TiO_2 on its photocatalytic performance. Whilst some studies have found a higher activity in the anatase form [5,6], others have reported the mixed phase anatase/rutile to show a better photocatalytic performance [7]. Comparative studies of single phase anatase and rutile TiO_2 have concluded that the photocatalytic activity is dependent on the reaction being studied and different kinetics and intermediaries may be produced in each case [8,9].

Due to its wide band gap, TiO_2 is only active under UV irradiation. It is possible to reduce the band gap of TiO_2 using one or more dopants to shift the activity to the visible range. The use of nitrogen as a dopant has been reported to result in enhanced visible light photocatalytic activity and hydrophilicity of TiO_2 [10,11]. Iron [12] and iron oxide [13] as well as a number of other dopants such as carbon nanotubes [14] and graphene [15] have been reported to increase the photocatalytic activity of TiO_2. Silver has been used both as a dopant to shift the activity of TiO_2 to visible light and as an antimicrobial agent [16–18].

TiO_2 and doped-TiO_2 films can be produced using a number of methods including sol-gel, chemical vapour deposition (CVD) and magnetron sputtering.

Reactive magnetron sputtering has several advantages over other coating methods such as sol-gel and CVD. Firstly, it eliminates the need to use the hazardous chemicals found in some of the other processes. Also, it is a versatile process in which, by varying the deposition conditions, both highly dense and porous columnar structures can be produced depending on the requirements. Furthermore, the deposition of double layer and multilayer coatings is easily achieved by the use

* Corresponding author. Tel.: +44 1905 827550; fax: +44 1905 827551.
E-mail address: Parnia.navabpour@miba.com (P. Navabpour).

http://dx.doi.org/10.1016/j.tsf.2014.10.040
0040-6090/

of different targets and rotation speeds [19]. Reactive magnetron sputtering has been widely investigated for the deposition of photocatalytic TiO_2 coatings. Several groups have described the effect of process parameters [20], such as total and oxygen partial pressures [21,22], deposition temperature [23], annealing [24] and doping [12,16] on the structure and photocatalytic properties of magnetron sputtered TiO_2. Deposition rates of up to 15 nm min^{-1} have been reported and unbalanced magnetron sputtering has been shown to produce a higher deposition rate than the balanced mode [25].

Closed field unbalanced magnetron sputtering (CFUBMS) is capable of producing coatings with high deposition rate and is readily scalable, making it a suitable process for the deposition of photocatalytic and self-cleaning coatings for industrial applications, such as food and beverage processing and medical devices. In this paper, we report on the deposition of TiO_2 and Ag-doped TiO_2 onto stainless steel substrates using reactive CFUBMS. The effect of process parameters on the coating structure, hydrophilicity, photocatalytic and mechanical properties, as well as the antimicrobial potential of the coatings were investigated.

2. Materials and methods

2.1. Preparation of coatings

TiO_2 and Ag-TiO_2 coatings were deposited using reactive magnetron sputtering in a Teer Coatings UDP 450 coating system. One or two titanium targets (99.5% purity) were used for the deposition of TiO_2. Argon (99.998% purity) was used as the working gas and oxygen (99.5% purity) as the reactive gas. An additional silver (99.95% purity) target was used for the co-deposition of silver during the process. Advanced Energy Pinnacle Plus pulsed DC power supplies were used to power the titanium targets and to bias the substrates. An Advanced Energy DC power supply was used to power the silver target. The substrate material was 304 stainless steel with a 2B finish (75 × 25 × 1.6 mm^3). All substrates were ultrasonically cleaned in acetone and dried prior to loading into the chamber in order to remove surface contaminants. The substrates were aligned on a flat plate parallel to the surface of the metal targets at a distance of 150 mm from the target plane. A high rotational speed of 10 rpm was applied to the substrates to ensure enhanced mixing of silver and titanium within the coatings rather than the preferential formation of multilayer coatings.

The substrates were ion-cleaned for a period of 20 min prior to the coating deposition using a bias voltage of −400 V and a low current of 0.2–0.35 A on the targets. The coatings were deposited at a bias voltage of −40 V. The amount of oxygen was controlled using an optical emission monitor and, to obtain stoichiometric TiO_2, the Ti metallic emission line intensity was set to 25% of the non-reactive deposition value. The deposition time was 60 min for all coatings.

2.2. Heat treatment

When used, post deposition heat treatment of the samples was carried out at 600 °C in air using a Prometheus kiln for 30 minutes, after which they were taken out of the kiln and cooled down at room temperature.

2.3. Characterisation of the coatings

Scanning electron microscopy (SEM) (Cambridge Stereoscan 200) was used to investigate the morphology of the coatings. An acceleration voltage of 15 kV was utilised. The composition and elemental distributions of the coatings were investigated using a SAMX energy dispersive X-ray analyser (EDX) system, attached to the SEM. The composition was measured on a minimum of five locations and the mean $\pm 2\sigma$ values were reported. High resolution SEM images were obtained using a JEOL 7000 Field Emission SEM (FE-SEM) at an acceleration voltage of 10 kV.

Raman spectroscopy (Renishaw Invia, 514 nm laser) and X-ray diffraction (XRD) (Bruker D8 Advance X-ray Diffractometer) were used to evaluate the crystal structure of the coatings. XRD measurements were performed using a Cu K_α radiation ($\lambda = 0.154$ nm) in 2θ steps of 0.014°, and a low scan speed of 0.01° s^{-1}.

2.4. Mechanical properties

The scratch and wear resistance of the coatings were assessed using a Teer ST3001 scratch–wear tester [26]. The coated surfaces were evaluated using a Rockwell diamond tip (radius 200 μm). A load rate of 100 N min^{-1} and a constant sliding speed of 10.0 mm min^{-1} were used with the load increasing from 10 to 40 N. The scratch tracks were examined using SEM in order to detect any flaking.

2.5. Contact angle measurements

Advancing drop contact angle measurements with water were carried out at room temperature on the as deposited coatings using a contact angle measuring instrument developed in-house. At least 6 measurements were taken for each surface and the reported values are mean $\pm 2\sigma$.

2.6. Photocatalytic properties

The photocatalytic activity of coatings was determined via the degradation of an organic dye — methylene blue (MB) (Alfa Aesar, UK). MB is a heterocyclic aromatic dye with a molecular formula of $C_{16}H_{18}ClN_3S$, and is often used as a model organic compound to measure photoreactivity [27,28]. Aqueous MB absorbs light most strongly at about 664 nm wavelength. The absorbance at 664 nm is proportional to the concentration, C, of MB, according to the Beer-Lambert law. A graph of C/C_0 against irradiation time can, therefore, be plotted which has an exponential form [29].

The coated substrate was inserted into 10 ml of MB solution (concentration of 0.105 mMol/l) and left in the dark for 30 min to allow the equilibrium adsorption level of the dye on the surface to be reached. The surface was then irradiated with 2 × 15 W fluorescent tubes at an integrated power flux of 6.4 mW/cm^2 (of which the UV component (300–400 nm) was 1.3 mW/cm^2) for 5 h. The beaker was covered with cling film to avoid evaporation of the solution which could otherwise affect the concentration and peak absorbance of the MB solution. Optical absorbance measurements of the MB solutions were taken every 1 h.

2.7. Antimicrobial assays

For the antimicrobial assays, an illuminated cooled incubator (Gallenkamp, Loughborough, UK) was used. The incubator was fitted with six fluorescent lamps (Sylvania, Ontario, Canada) with a wavelength

Table 1
Parameters used for the deposition of TiO_2 and Ag-TiO_2 coatings.

Coating	Ti (A)	Ti (-V)	Ag (A)	Ag (-V)	Thickness (μm)	Deposition time (min)
Ti-I Coatings						
Ti1	1 × 6	1 × 410	0.00	0	1.0	40
Ti1-Ag1	1 × 6	1 × 390	0.25	300	1.1	40
Ti1-Ag2	1 × 6	1 × 390	0.60	330	1.9	40
Ti-II Coatings						
Ti2	2 × 6	2 × 415	0.00	0	2.0	60
Ti2-Ag1	2 × 6	2 × 415	0.50	215	2.0	60
Ti2-Ag2	2 × 6	2 × 415	0.70	230	2.1	60
Ti2-Ag3	2 × 6	2 × 430	0.90	330	3.0	60