HiPIMS Deposition of Tungsten-doped Titania Coatings for Photocatalytic Applications

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Abstract

Tungsten-doped titania coatings have been deposited from a Ti-5 at% W alloy target in HiPIMS mode. The coatings were weakly crystalline and showed mixed anatase/rutile structures in the as-deposited condition. Their photocatalytic activity was assessed in terms of the degradation rate of methylene blue dye. The W-doped coatings showed no improvement in activity, compared to pure titania coatings under UV irradiation, however under fluorescent and visible light sources, the activity was significantly enhanced. This was attributed to a red-shift in the band gap energy of the doped coatings.

1. Introduction

Titania coatings produced by magnetron sputtering are widely described as photocatalysts, however they typically require post-deposition thermal treatment for the development of the required crystal structure. In particular, the anatase phase of titania, reportedly the most active phase in terms of photocatalytic behaviour, develops at annealing temperatures of around 400 ^{0}C [1]. This significantly limits the choice of materials that may be used as a substrate for these photocatalytic coatings and imposes further processing costs. Throughput could be improved and processing costs reduced if the coatings could be deposited in a single stage process.

High power impulse magnetron sputtering (HiPIMS) is a deposition technique that utilizes high peak powers over short pulse times to provide high density, highly ionised plasmas, which enable the deposition of dense crystalline coatings at low temperatures [2]. This technique has been shown to be suitable for the deposition of photocatalytic titania coatings onto a variety of substrates, including polymeric films [3]. However, as expected for pure titania coatings, these thin films show photocatalytic properties only under UV light irradiation, as the band gap of anatase titania is typically 3.2 eV. Doping is a well-known and promising technique for shifting the photocatalytic activity of titania towards the visible range [4, 5]. Transition metal ions of similar ionic radii to titanium have been shown to occupy substitutional positions in the titania lattice, thus extending the lifetime of photogenerated charge carriers [6]. Doped titania coatings can be produced by co-sputtering from a titanium target and a dopant target [4]. However, multi-source HiPIMS deposition systems are still under development and it is not currently possible to produce doped titania coatings by sputtering two (or more) targets simultaneously in HiPIMS mode. Furthermore, the combination of DC or pulsed DC power supplies with a HiPIMS supply is not desirable due to the risk of damage to the former supplies.

Sputtering an alloy target of known composition in HiPIMS mode does, though, provide a route to producing doped titania coatings in this mode. In the present work a titanium-tungsten alloy target (Miba Coatings Ltd. UK) with 5 at. % of W was used for production of W-doped titania coatings in HiPIMS mode. W-doping of titania coatings is reported to extend the lifetime of photogenerated charge carriers, as well as shifting the band gap of the photocatalyst towards the visible range [4, 7]. The content of tungsten in the target was based on the information obtained for pulsed DC coatings produced previously, where 5-6 at. % W was shown to be an optimum concentration for photocatalytic activity enhancement [4]. This work evaluates the use of an alloy target in HiPIMS mode for the deposition of W-doped titania coatings. Undoped titania coatings were produced under identical condition for reference purposes using a pure titanium target (99.5% purity).

The coatings were deposited in a Nordiko sputtering rig fitted with a single 300 mm × 100 mm unbalanced magnetron. The alloy target was bonded to a copper backing plate and mounted on the magnetron (Gencoa Ltd., UK), which incorporated thicker insulation compared to regular planar magnetrons to prevent arcing and breakdown. The magnetron was powered using a Huettinger HMP1/1_P2 HiPIMS power supply. All the coatings were produced using a pulse frequency of 200 Hz and pulse width of 100 μs. The mean power during the pulse was varied from 30 to 44 kW (equivalent to time averaged powers of 600W and 880W, respectively). The sputtering was carried out in an argon : oxygen atmosphere at a pressure of 0.33Pa, with the flow of gases controlled through mass flow controllers and fixed as 2 : 3, respectively, for all deposition runs. Soda lime glass substrates were mounted on rotatable drum-shaped substrate holder at 10 cm distance from the target. The target waveforms (current, voltage and delivered power) were monitored with a Tektronix digital oscilloscope.

The composition of the deposited coatings was analysed with energy dispersive X-ray spectroscopy (EDX) (EDAX Trident, installed on a Zeiss Supra 40 VP-FEG-SEM). Information on the crystal structure of the deposited coatings was obtained with Raman spectroscopy (Renishaw Invia, 514 nm laser). The surface roughness and surface area of the coatings were measured with a MicroXAM white light surface profilometry. Band gap values for the coatings were calculated using the Tauc plot method. Photocatalytic properties of the coatings were assessed using the methylene blue (MB) degradation photocatalytic test, under both UV (2×15W 352 nm Sankyo Denki BLB lamps) and fluorescent light (2×15W Ushio fluorescent lamps) sources. The MB aqueous solution absorption peak height at 665 nm was monitored continuously for 1 hour using an Ocean Optics 2000+ spectrometer. The first order reaction constant, k_a, was used as the value of absorption decay rate and calculated from the gradient of the plot of $\ln(A_0/A)$ against time (A_0 is absorption value at time 0, A is absorption value at the time of experiment). The potential effect on k_a of MB absorption on the surface of the photocatalyst was excluded by pre-immersing the samples prior to the photocatalytic measurement in a conditioning solution of MB for 30 min. The measurements of photocatalytic activity were carried out using 40 ml of MB solution (concentration 1.5 μmol/l). The natural decay rates of MB in the dark and under both light sources without contact with a photocatalytic surface were measured for reference purposes. In 1 hour experiments, these values were all of zero order, thus could be neglected in the reaction constant calculations. Therefore any changes in MB solution absorption peak height were attributed to the photocatalytic activity of the coatings.

An overview of the deposition conditions and measured parameters of the coatings is given in Table 1.

Table 1. Overview of deposition conditions and properties of the titania and W-doped titania coatings deposited on glass substrates

Coating ID	Mean sputtering power, kW	W, at. %	Band gap, eV	Surface roughness, µm	Surface area, µm^2	$k_a \times 10^5$, UV light, s^{-1}	$k_a \times 10^5$, fluorescent light, s^{-1}	$k_a \times 10^5$, visible light, s^{-1}
T1	30	---	3.22	0.070	5523	2.4	0.5	---
T2	44	---	3.21	0.084	5521	2.0	0.3	---
TW1	30	6.02	3.07	0.087	5521	2.0	1.0	0.9
TW2	44	5.67	3.04	0.092	5524	2.1	1.2	0.9

The results of EDX analysis showed that the W-doped coatings had tungsten contents of between 5.6 and 6 at. %. i.e., very similar to the composition of the target. The results of Raman spectroscopy are shown in Figure 1. All the Raman spectra obtained corresponded to nanocrystalline coating structures [8]. They showed that all the coatings exhibited some degree of crystallinity, in the form of mixed anatase and rutile phases. However the peaks were sharper and better defined in the Raman spectra of the undoped titania coatings, compared to the W-doped coatings. A strong peak seen at 1100 cm^{-1} can be atributed to titanium – oxygen – silicon dioxide bond formation, which may be taken as an evidence of strong interaction between the glass substrates and the coatings [9].

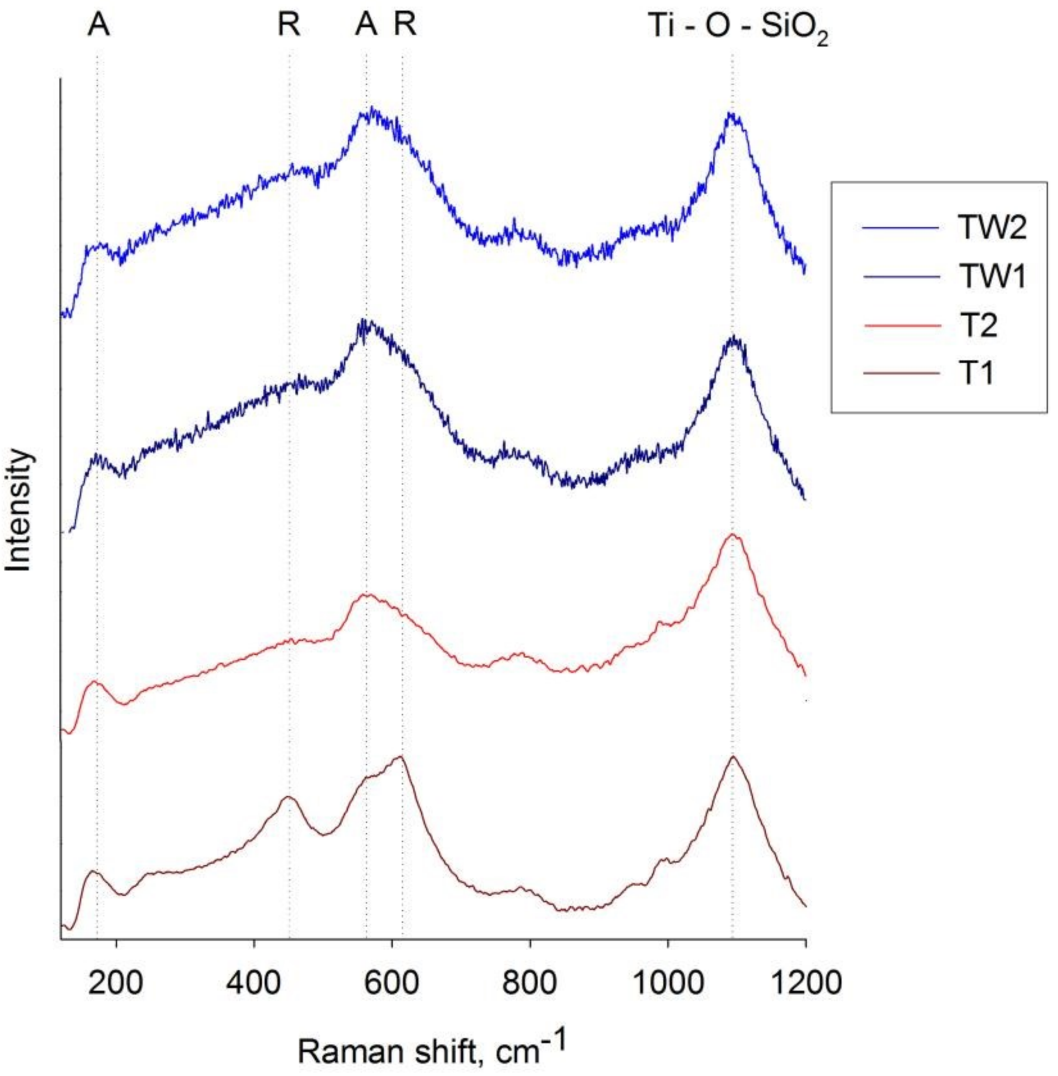

Figure 1. Raman spectra of W-doped and undoped titania coatings deposited by HiPIMS on glass substrates

Surface topography measurements showed that the roughness and surface areas were not modified significantly by introducing tungsten to the coatings. All of the coatings studied were characterised with relatively low surface roughness values, ranging from 0.07 to 0.09 μm.

The calculation of the band gap indicated a considerable shift of the band gap value towards the visible range for the W-doped coatings, compared to the undoped titania coatings. Some examples of band gap calculation are shown in Figure 2, and the estimated band gap values are given in Table 1. A significant shift of the band gap for the doped coatings would be expected to improve the photocatalytic activity under a fluorescent or visible light source.

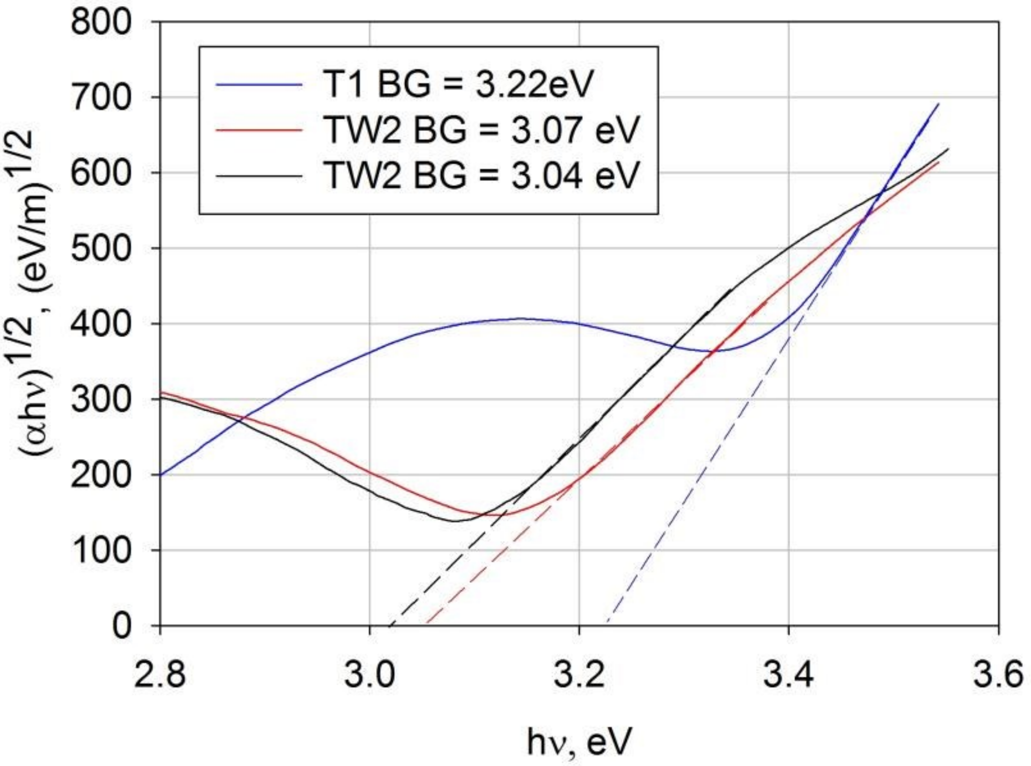

Figure 2. Estimation of the band gap values for W-doped and undoped titania coatings deposited by HiPIMS

The photocatalytic measurements using MB decomposition were carried out for all the coatings and the results are reported in Table 1. It can be seen that UV light activity for the doped coatings was similar or slightly lower than the pure titania coatings. However, under the fluorescent light source, the activity of the undoped coatings was of very low (almost negligible), as expected, since the band gap of the titania coatings was around 3.2 eV, whereas the W-doped coatings showed noticeable activity (~50% of UV level). To ensure that the degradation of MB observed for the W-doped coatings was caused by the visible portion of the fluorescent light spectrum, rather than its UV component, a 395 nm long pass UV filter (Knight Optical) was used to block the UV component. The visible light MB degradation rate constant values obtained for the W-doped coatings were only slightly lower than for fluorescent light experiments, indicating that the doped coatings still exhibited an ability to degrade methylene blue under visible light.

In summary, based on the results presented here, it can be concluded that sputtering an alloy target in HiPIMS mode presents a convenient way of depositing crystalline doped titania coatings in a single stage process, without the requirement for further thermal treatment. Varying mean power from 30 to 44 kW did not have a significant effect on the coating properties. It was further shown that the tungsten inclusion in the titania coatings resulted in a 'red-shift' of the band gap towards the visible range and, therefore, increased photocatalytic activity under a fluorescent or visible light source. However, the presence of tungsten was also shown to inhibit the crystal phase growth, compared to the pure titania films.

Despite the absence of photocatalytic activity enhancement under UV light irradiation, the W-doped coatings had a significant advantage in their ability to degrade methylene blue under fluorescent light and visible light. This opens the door to possible applications of these coatings in indoor photocatalysis. In addition, as the HiPIMS coatings do not require thermal treatment for crystal structure development, they can be deposited onto a wide range of substrates, including temperature-sensitive ones, such as plastics. This further expands the choice of potential applications for these coatings.

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