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Deposition of photocatalytic TiO_2 layers by pulse magnetron sputtering and by plasma-activated evaporation

P. Frach*, D. Glöß, Chr. Metzner, T. Modes, B. Scheffel, O. Zywitzki

Fraunhofer-Institut für Elektronenstrahl- und Plasmatechnik (FEP), Winterbergstr. 28, 01277 Dresden, Germany

Abstract

Crystalline TiO_2 thin films, especially layers with predominantly anatase phase, exhibit photocatalytic activities resulting in photoinduced hydrophilic, self-cleaning and antifogging properties. In this paper, a comparison of the photocatalytic properties of layers deposited with two different PVD techniques is given.

On one hand, a reactive pulse magnetron sputtering (PMS) system has been used to obtain TiO_2 films at dynamic deposition rates from 8 to 50 nm m/min. On the other hand, TiO_2 layers were deposited by reactive electron beam evaporation at very high deposition rates between 500 and 1000 nm m/min. An additional spotless arc discharge (Spotless arc Activated Deposition—SAD process) was used for plasma activation to improve layer properties. Photoinduced hydrophilicity was investigated by measuring the decrease of the water contact angle during UV-A irradiation.

Keywords: Titanium dioxide; Photocatalysis; Pulse magnetron sputtering; Reactive sputtering; Plasma-activated reactive evaporation; Low-temperature deposition

1. Introduction

The photoinduced hydrophilic and photocatalytic behaviour of TiO_2 films with the anatase phase allows to create products with new properties like easy-to-clean surfaces, self-cleaning windows, antifogging glass, antibacterial tiles or photocatalytic air cleaning and water purification devices. A lot of applications require a high rate deposition technique and upscaling capability because of the large surfaces to be coated at low costs. The aim of this work is to use and compare two PVD methods for high rate deposition of crystalline TiO_2 films [1–4]: reactive medium frequency pulse magnetron sputtering (PMS) and plasma-activated evaporation.

For the PMS technique, it is known that the pulse mode significantly influences the particle bombardment onto the growing film [5] and opens up a way to deposit crystalline TiO_2 films at reduced temperature [4]. A comparison of the photocatalytic properties of TiO_2 layers deposited using different pulse modes will be presented. Another goal was the deposition of thin TiO_2 films (<50 nm) at low substrate temperatures with sufficient photocatalytic activity.

A further increase of deposition rate can be achieved by reactive electron beam evaporation. Still, for a broad application, the layer quality mainly in respect of packing density has to be improved. By plasma activation using spotless cathodic arc (Spotless arc Activated Deposition—SAD), a higher energy of condensing particles can be achieved [6].

2. Characterization of layer properties

The structure of the films was characterized by X-ray diffraction (Bruker-AXS, D8 Advance) using Cu Kα radiation and grazing angle of incidence of 1°. The anatase and rutile proportions in the layers were estimated using intensities of reflexes and an empirical equation published by Spurr and Myers [7]. The photoinduced hydrophilicity of the films was investigated by measuring the contact angle of water (G-23E from Krüss GmbH) after irradiation

*Corresponding author. Tel.: +49 351 2586 370; fax: +49 351 2586 55 370.
E-mail address: peter.frach@fep.fraunhofer.de (P. Frach).

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with ultraviolet light (Philips TL-DK 30 W/05; $P_{UV\text{-}A} = 1\,mW/cm^2$).

3. Pulse magnetron sputtering

3.1. Experimental

A reactive PMS system allowing to change the pulse mode and the duty cycle has been used for the sputter deposition of TiO_2 films. This system developed and manufactured by the Fraunhofer-Institut für Elektronenstrahl- und Plasmatechnik (FEP) consists of two flange-mounted magnetrons (target: Ti), a switching unit (UBS-C2) to generate the pulse powering, gas control devices and a process management computer for complete automatic control. In the unipolar pulse mode, both targets act as cathode of a separate discharge using the hidden anodes of the magnetrons as counter electrode. In the bipolar pulse mode, each of the targets of the two magnetrons acts alternately as cathode and anode of the bipolar discharge. A further development of the bipolar pulse mode is the pulse packet mode. Each packet consists of a selected number of unidirectional pulses. The next packet consists of a selected number of unidirectional pulses of the other polarity. The pulse packet mode ensures a higher process stability even in the case of occurring arcs. Details of the function of the PMS system and the pulse modes are described elsewhere [4,5].

The layers were deposited in the pass-mode (moved substrates) of an in-line deposition plant. Substrate was float glass (soda lime) with thickness of 3 mm. Important deposition parameters are summarized in Table 1. The total pressure had been kept constant at 0.7 Pa. The discharge power was adjusted to 10 kW per target ($400 \times 130 \times 10\,mm^3$) for all experiments (power density: $18.2\,W/cm^2$).

The experiments were carried out on one hand by stabilizing the reactive sputtering process at a reactive working point in the transition mode between the metallic and the reactive sputter mode close to the transparency limit, i.e. at the highest rate for absorption-free layers. A closed-loop control was used for the reactive gas inlet to keep the optical emission intensity of the Ti line (500 nm) at a constant value. By changing the pulse mode (unipolar, pulse packet and bipolar for samples 1, 2 and 3, respectively), the substrate bombardment by energetic plasma particles (plasma impact) can be adjusted [8].

On the other hand, investigations regarding the deposition of thin photocatalytic TiO_2 layers at even lower substrate temperatures were carried out. By choosing a more reactive working point, a very high substrate bombardment was achieved (samples 4–6).

The relative thermal substrate load (Table 1) was evaluated (according to [5]) by measuring the substrate temperature raise during deposition of films with thickness of 100 nm (with process parameters identical to that of samples 1–3) or 45 nm (sample 4). Referring to the same film thickness, the differences in the thermal load are caused only by different plasma impact strength only. Furthermore, we observed that even in the unipolar pulse mode, about 70–80% of the thermal load is caused by the plasma impact [9]. Therefore, the thermal load can be taken as a measure of the plasma impact for different process parameters.

3.2. Results and discussion

In the unipolar pulse mode, the temperature during deposition of a 100 nm TiO_2 layer enhances by 28 K—corresponding to a relatively low plasma impact (sample 1 in Table 1). In the pulse packet mode and the bipolar pulse mode, the temperature raise amounts 51 and 57 K, respectively, corresponding to a medium plasma impact (roughly factor 2 for samples 2 and 3 in comparison to unipolar pulse mode). This confirms the results described in [5]. Applying the pulse packet mode and a more reactive working point, the temperature raise during deposition of 45 nm TiO_2 amounts 103 K. Referring to the same film thickness, a high plasma impact was achieved (roughly, factor 8 for samples 4–6 in comparison to unipolar in transition mode).

Fig. 1 displays XRD patterns of layers deposited using low and medium plasma impact. Broad and relative small diffraction peaks of rutile phase superimposed with a broad amorphous scattering peak can be recognized for the layer deposited in the unipolar pulse mode (sample 1, Fig. 1). It is therefore probably that the growth of this layer starts with deposition of amorphous phase, whereas at

Table 1
Deposition parameters for pulse-magnetron-sputtered TiO_2 layers used in this investigation

Sample	1	2	3	4	5	6
Pulse mode	Unipolar	Pulse packet	Bipolar	Pulse packet	Pulse packet	Pulse packet
Duty cycle	80%	40%	45%	40%	40%	40%
Dynamic deposition rate (nm m/min)	51	47	39	8	8	8
Layer thickness (nm)	500	500	500	45	85	170
Pre-heating (°C)	200	200	200	No (RT)	No (RT)	No (RT)
Maximum deposition temperature (°C)	230	240	240	130	180	250
Relative thermal load	1	2			8	
Plasma impact	Low	Medium			High	