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Photo activated performance of titanium oxide coatings deposited by reactive gas impulse magnetron sputtering

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ABSTRACT

A novel reactive gas impulse magnetron sputtering (GIMS) technique was applied in order to deposit titanium dioxide coatings. A small volume magnetron sputtering reactor was used for that purpose, wherein titanium target was reactively sputtered under a pure oxygen atmosphere. The process resulted in a high quality nearly stoichiometric and fairly crystalline TiO_2 films with a prevailing content of rutile. The coatings exhibit a strong photowetting effect – it takes 25 min of illumination with UV-C radiation to arrive at their "superhydrophilic" behaviour. In addition, in the discussed process of reactive GIMS deposition of titanium dioxide films, no target poisoning effect has been observed.

1. Introduction

Photocatalytic activity of titanium (IV) oxide was first discovered in 1972 by Fujishima and Honda [1]. In brief, it consists in a substantial modification of this compound certain physical and chemical properties under the effect of ultraviolet (UV) light. Fujishima and Honda demonstrated the effect of UV irradiation of TiO_2 surface on catalytic decomposition of water remaining in contact with that surface [1]. Since then, a number of UV induced processes and activities of titanium dioxide have been reported, among others its bactericidal effect [2–5], oxidative power [6–8] and, last but not least, a phenomenon of photowetting [5, 9–11]. The latter effect consists in a substantial decrease of water contact angle of TiO_2 surface irradiated with UV light. Unexposed, titanium dioxide exhibits hydrophobic properties with the typical contact angle amounting to 80–100°. That angle decreases dramatically after the material's exposure to UV irradiation with a formation of a superhydrophilic surface – a process frequently utilized in photo-cleaning procedures [12].

A photo-cleaning process is based on two different phenomena: photocatalysis and photowetting. The former consists in an ability of TiO_2 coatings to oxidize adsorbed chemicals, both organic and inorganic, as a result of which they degrade to simple and harmless forms [6–8]. This effect is utilized in self-cleaning filters for water and air purification, for instance. As far as photowetting is concerned, it produces a thin film of water on a TiO_2 surface, and this film rinses off all the contaminants present on that surface [12–14]. Such a coating is utilized, among others, in solar cells to protect their surface against contamination. Another photo-cleaning application of TiO_2 comprises coatings that keep glass clear – a thin film of liquid water protects glass against fogging [14]. This application is often used in the automotive industry.

As indicated above, a common form of TiO_2 is a form of a coating. Typically, due to their simplicity and low costs, such coatings are produced with the help of sol-gel methods [15–19]. Other deposition techniques include: reactive sputtering [10, 20–22], spray pyrolysis [23], hydrothermal method [24] and plasma enhanced chemical vapor deposition [4, 5, 18, 19].

For some years, there has been an interesting novel modification of sputter deposition technique developed in Poland [25–28]. This method, called gas impulse magnetron sputtering (GIMS), consists in an application of a repeated pressure pulses of a working gas medium (controlled by an impulse needle valve) of a magnitude enabling an initiation of a glow discharge. With the closing of that valve, pressure drops beyond the level of discharge maintenance, and the glow is extinguished [25]. A subsequent opening of the valve restores the discharge. Such a procedure has a number of advantages. First of all, it should enable an application of high power density peaks and, therefore, an increase of the concentration of ionized species [26]. This, in turn, favors a formation of compact coatings on complicated surfaces. Secondly, in contrast to conventional reactive magnetron sputtering, this technique allows one to work with pure oxygen. In addition, it also eliminates target poisoning.

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The GIMS technique has already been applied to the synthesis of titanium dioxide coatings by Skowronski et al. [27] and by Zdunek et al. [28]. In the former work, the authors use TiO_2 as a model material synthesized in order to compare two different pulsed PVD procedures: pulse magnetron sputtering (PMS) and the GIMS method [27]. They report the coatings deposited with the GIMS technique to exhibit substantially higher values of hardness and elastic modulus than those of PMS samples. As opposed to the latter method which favors a formation of anatase, in the coatings synthesized with the PMS technique the authors find mostly rutile crystalline phase. Apart from mechanical properties they also report optical characteristics of the coatings but not their photocatalytic and photowetting properties. What is more, in their next publication reporting an industrial scale GIMS deposition of titanium dioxide coatings on large (2000 × 3000 mm) glass sheets, the authors underline decorative functions of the coatings without any reference to their self-cleaning properties [28]. Therefore, the present work should fill the gap by presenting the photo induced activity of the titanium dioxide coatings synthesized with the GIMS method. Apart from that, an obvious advantage of a substantial lowering of the target poisoning effect by using this method is also discussed.

2. Materials and methods

2.1. Deposition reactor

A self-constructed small volume magnetron sputtering reactor has been used in this work. A cylindrical deposition chamber of the dimensions d = 100 mm and h = 125 mm, equipped with a rotating sample holder and electrically isolated driving mechanism enabling polarization of the substrates, constitutes a core of that reactor. Vacuum supply system of the reactor consists of mechanical and diffusion pumps and a set of electromagnetic valves which allow one to maintain a base pressure in the deposition chamber of the order of magnitude of 10^{-3} Pa. The upper cover of the deposition chamber is equipped with titanium magnetron target of a diameter equal 25.4 mm, coupled with the Pulse-DC type of power supply. The main part of the sputtering unit is a gas needle valve enabling a creation of very short gas pulses (opening time amounting to milliseconds) with repetition frequency between 0.5 and 10 Hz. The vacuum unit is equipped with a gas supply line working in continuous mode with standard mass flow meters (10 sccm). A schematic representation of the reactor is presented in Fig. 1.

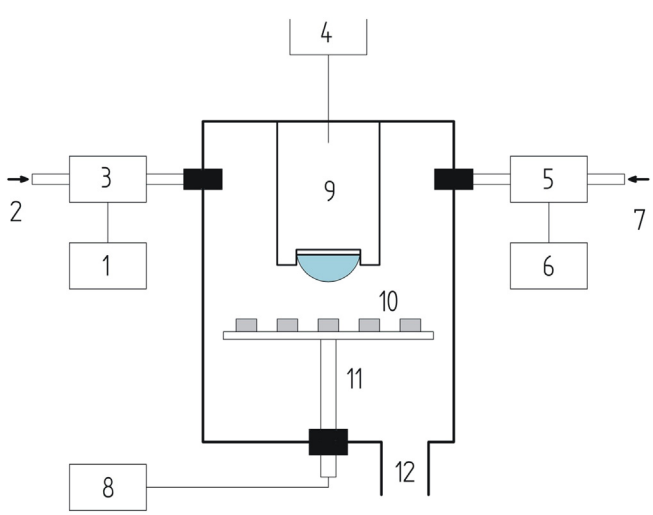

Fig. 1. A schematic representation of the low volume magnetron sputtering reactor with the impulse gas valve controller (1), oxygen inlet (2), impulse gas valve (3), magnetron power supply (4), mass flow regulator (5), flow controller (6), argon inlet (7), bias (8), magnetron with 1″ diameter target (9), samples (10), rotating table (11) and pumps (12). Diameter of sample holder: 88 mm.

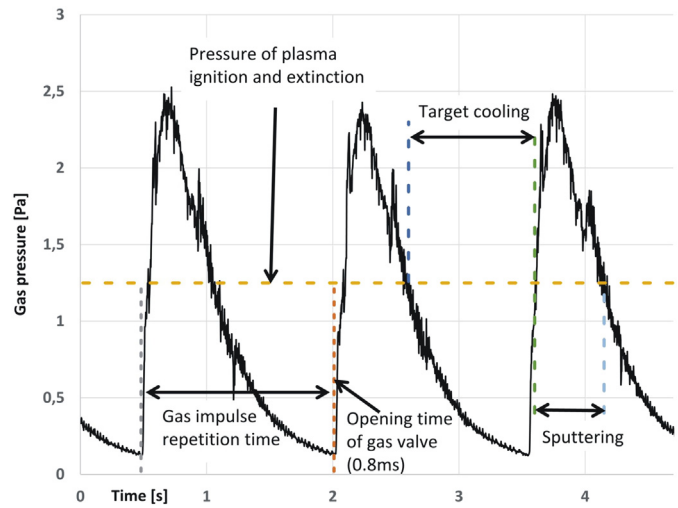

Fig. 2. A profile of periodic pressure changes in the gas impulse magnetron sputtering process.

2.2. Gas impulse magnetron sputtering

The gas impulse sputtering mode is realized in the following way. The principle idea is to generate, at infrasound frequency, short (of an order of magnitude of milliseconds) gas pressure impulses of a magnitude enabling an initiation of a glow discharge in the reactor. With the continuously working vacuum system, periodic changes of pressure in a form of pulses are created, thus initiating and extinguishing plasma in the chamber with the same periodicity. As a result, an intensive magnetron discharge of high plasma density accompanied by emission of high intensity visible light is observed in the chamber. A typical pattern of pressure changes in the chamber is presented below, in Fig. 2.

2.3. Deposition of the coatings

Round pieces of titanium alloy Ti6Al7Nb of a diameter equal 8 mm and thickness equal 5 mm were used as substrates in this work. Prior to their placement in the deposition chamber, the substrates had been subjected to grinding and polishing procedures followed by ultrasound rinsing in acetone for 10 min. The former procedure comprised grinding with sandpaper of grain gradation increasing between 20 and 2400, while polishing was carried out with the help of automatic Presi MECATECH 334 polishing device. Apart from metallic substrates, 500 μm thick, p-type silicon wafers of the orientation of ⟨100⟩ were also used as the coating support. A distance between the substrates and the target amounted to 25 mm.

Each deposition of titanium oxide coating was preceded with argon plasma etching of the substrate surface. In contrast to the deposition process performed in a gas pulse mode, argon etching was carried out in a continuous manner. The following were the etching parameters: argon working pressure equal 4 Pa, voltage equal 1.3 kV with the resulting current equal nearly 50 mA. A duration of argon etching process was 1800 s. The detailed parameters of titanium oxide deposition process are, in turn, presented in Table 1, below.

2.4. Characterization of the coatings

2.4.1. X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) measurements were performed using Kratos AXIS Ultra XPS spectrometer equipped with a monochromatic Al Kα X-ray source of excitation energy equal 1486.6 eV. The spectra were collected from an area of