



Bactericidal and photowetting effects of titanium dioxide coatings doped with iron and copper/fluorine deposited on stainless steel substrates



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ABSTRACT

Titanium dioxide coatings, doped either with Fe or with a Cu/F combination, were deposited onto 316 LVM steel with radio frequency plasma enhanced chemical vapor deposition technique. As a source of titanium, titanium (IV) chloride was used, while iron pentacarbonyl and copper(II) (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) served as precursors for iron and copper/fluorine, respectively. The coatings were evaluated in terms of their surface topography using atomic force microscopy, phase composition using low angle X-ray diffraction and chemical composition using both Raman and Fourier transform infrared spectroscopies. Mechanical properties, such as adhesion, hardness and Young modulus, were tested. Finally, bacteriostatic and bactericidal properties of the films as well as their water wettability under ultraviolet light illumination were assessed. The coatings had primarily amorphous structure, with the exemption being those containing 0.5 and 1.4 atomic % of iron, where anatase/rutile and rutile reflexes were recorded, respectively. Mechanical properties of the films were found to be satisfactory and their bactericidity substantial.

1. Introduction

Due to its UV induced photocatalytic activity, titanium dioxide (TiO₂) is used in a broad spectrum of applications comprising various environmental and health care procedures [1,2]. When excited, this material exhibits strong oxidizing properties affecting both organic and inorganic chemicals, and it has a destructive impact on bacteria, viruses, algae, fungi and moulds [3–5]. A simultaneously recorded photo-wetting effect consists in the ability of its surface to turn super-hydrophilic under an ultraviolet (UV) light illumination [6,7]. This results in rinsing all solid particles and other contaminants off that surface in a self-cleaning process, whenever it becomes sprinkled with water. In addition, titanium dioxide is characterized by good biocompatibility, chemical stability and corrosion resistance [8,9].

In the literature reports, TiO₂ coatings are deposited either onto glass (including quartz) [10] and monocrystalline silicon substrates [11,12] when aimed at the assessment of their composition and chemical structure or, in particular applications, onto such substrates as polymer foil [13], textile [14] and metal plates [11,15,16]. A use of the latter substrates allows one to substantially broaden the scope of applications, among others, into the area of implants and medical appliances. It is of particular importance today, at the time of a widespread overuse of antibiotics and strong mutagenic disinfection chemicals that

leads to various microbiological risks. Therefore, a search for novel alternative means of antibacterial protection is underway. An inhibition of the growth and multiplication of microorganisms and, therefore, a reduction of microbiological hazards, may be for instance achieved by an application of self-cleaning and self-disinfecting coatings on reusable medical tools and appliances [17].

A bactericidal effect with no excitation is exhibited by a number of metals such as copper [18], silver [19], gold [20], platinum [21] and zinc [22]. Unfortunately, some of these materials are expensive while others induce serious allergic responses. Another argument against a use of metallic coatings on steel substrates, either austenitic or martensitic, comprises a formation of corrosion stimulating bimetal systems. These are reasons why a bactericidal TiO₂ coating, which at the same time may protect the bulk material against corrosion, appears to be a promising solution [9].

Films of titanium dioxide, both plain and doped with various elements, may easily be synthesized with a number of methods. The most popular of these methods comprise: sol-gel technique [11,18], chemical vapor deposition (CVD) with its modification of metalorganic vapor deposition (MOCVD) [19], physical vapor deposition (PVD) with a predominant magnetron sputtering method [20], electrodeposition, hydrothermal deposition [21] and anodization [22]. The plasma enhanced chemical vapor deposition (PECVD) technique has been pointed

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to, among others by our research group, as a method suitable for a synthesis of titanium dioxide intended for both optical and photocatalytic applications [13,14,23,24]. However, it should be stressed that doping of PECVD films with minority elements constitutes a difficult task and a number of respective publications is rather limited. One frequent limitation comprises an availability of the precursors. Under normal conditions, a substance constituting a source of dopant remains in one of the three possible states of aggregation. An addition of gaseous source materials can be easily controlled by needle valves and these materials can be introduced directly into the discharge zone. As opposed to that, precursors remaining in condensed phases require evaporation, which involves a necessity to apply heat and to control temperature and/or vapor pressure. Obviously, the former situation requires the simplest experimental set-up. This is greatly a reason why nitrogen makes a very popular non-metallic dopant of titanium dioxide. For example, Cho et al. have characterized TiO_xN_y coatings of different contents of nitrogen. These coatings were deposited on silicon Si(100) substrates with a use of titanium isopropoxide $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ (TTIP) as Ti precursor and gaseous N_2 as a source of nitrogen. The authors investigated the effect of nitrogen content in the films on their chemical structure, phase composition, morphology and hardness. Such films find broad applications as anticorrosion coatings on jewelry products and, because of their excellent optical properties, also as optical filters. In addition, due to high optical gap value, they also serve as photocatalysts [25]. In the works of Maeda et al., N-doped TiO_2 films were prepared by the radio frequency PECVD technique, using argon carried TTIP and NH_3 as the precursors. In these coatings, which exhibited crystalline structure of anatase, nitrogen atoms substitute oxygen and their principal application is photocatalysis [26]. In another work, Youssef et al. have reported titanium dioxide coatings deposited on silicon (100) wafers and on borosilicate strips with an application of a low-frequency PECVD reactor using TTIP in a mixture of Ar and O_2 as the TiO_2 precursor. The source of nitrogen was comprised of a mixture of ammonia an N_2 . A use of the two operational parameters (substrate temperature and discharge power) of the synthesis allowed the authors to deposit coatings of anatase structure that stimulated a strong photocatalytic degradation of stearic acid [27].

Another admixture, intentionally introduced into the TiO_2 structure in a PECVD process is boron, reported by Quesada-Gonzalez et al. As precursors, the authors used titanium ethoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$), and boron isopropoxide ($\text{B}[(\text{CH}_3)_2\text{CHO}]_3$), while the films were deposited on photo illuminated PMMA optical fibers [28]. Atmospheric pressure PECVD technique was also used for the purpose of deposition of TiO_2 coatings with an admixture of SiO_2 . Gazal et al. have characterized such materials synthesized from a TTIP and hexamethyldisiloxane (HMDSO) mixture on silicon substrates. By changing the torch to substrate distance the authors were able to alter the TiO_2 structure from amorphous to that of anatase, with the SiO_2 structure remaining amorphous. In addition, a formation of Ti-O-Si bonding enhanced a photocatalytic activity of the coatings [29]. Similar material, also characterized by good optical properties, was obtained by Li et al. [30]. In their work, Gracia and coworkers, compared the effect of ion beam induced CVD (IBICVD) and PECVD procedures on the crystalline structure and optical properties of bare TiO_2 coatings and the same coatings doped with vanadium. As a source of titanium, either titanium (IV) chloride (TiCl_4) or TTIP were used, while vanadium (V) oxychloride (VOCl_3) served as the vanadium precursor. The coatings were deposited on quartz, silicon or metal plates [31]. Lin and coworkers indicate in their article that oxygen vacancies indeed play a positive role in the ferromagnetic coupling between Co^{2+} ions in $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ systems, synthesized on silicon (001) substrates by PECVD method from bis(cyclopentadienyl) titanium(IV) dichloride ($\text{C}_{10}\text{H}_{10}\text{TiCl}_2$) and cobalt (III) 2,4-pentandionate ($\text{C}_{15}\text{H}_{21}\text{O}_6\text{Co}$) as the source materials for Ti and Co, respectively [32].

In general, a precise doping of RF PECVD synthesized titanium dioxide coatings in a single process appears problematic. This is a reason

why the process is often split in two parts: chemical vapor deposition for a synthesis of the coating and another technique for its doping. A good example of such an approach is presented by Hajkova et al., where TiO_2 coatings were deposited on glass substrates from TTIP by the conventional RF PECVD technique and they were later enriched with silver using a PVD method with a simultaneously performed chemical reduction. The coatings exhibited a bactericidal effect on Gram-negative bacteria *E. coli* [33]. Another example is given in the work of Carraro et al. [32], where nanocomposite coatings of the $\text{Fe}_2\text{O}_3\text{-TiO}_2$ type were obtained on active carbon fibers (ACFs) with a use of a two-stage procedure: plasma enhanced chemical vapor deposition (PECVD) of iron oxide followed by radio frequency titanium sputtering. Such a coating may find an application either in photoactivated systems for catalytic generation of hydrogen or as photo-oxidizing agent of organic contaminants [34]. Our group (i.e. that of A. Sobczyk-Guzenda and her co-workers), in a number of publications, has reported in detail a method of RF PECVD synthesis of TiO_2 coatings doped with iron (Fe^{3+}). For that purpose, we used titanium (IV) chloride TiCl_4 as titanium precursor and iron pentacarbonyl $\text{Fe}(\text{CO})_5$ as a precursor of iron [35–37]. In one of our the latest publications we also reported results of a double doping of TiO_2 coatings with copper and fluorine with an application of copper (II) (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) as a source of both additives [38].

The present work constitutes a continuation of our studies on TiO_2 coatings synthesized with the RF PECVD method. In this work, iron doped coatings and those doped with copper and fluorine at three particular concentrations were selected on the basis of our earlier experience, with the 316 LVM steel this time used as a substrate material for depositions. As a result, a strong influence of the steel substrate on chemical structure and phase composition of the resulting coatings and, therefore, also on their photowettability and bactericidity was observed compared to the earlier results obtained for similar films deposited on quartz and silicon substrates [35–38]. In addition, the effect of the type of admixture and that of its content on such principal mechanical parameters of the films as their adherence and hardness were also assessed. All that information substantially broadens the topic of doped titanium dioxide coatings in general.

2. Experimental

2.1. Materials

SANDVIK BIOLINE 316 LVM (ISO 5832-1) austenitic steel discs having 16 mm diameter and 5 mm height were used as substrates. They were polished with Struers DiaPro PLUS3 diamond polishing paste of a grain size of 3 μm . After polishing, the substrates were rinsed in an ultrasound washer for 15 min using ethyl alcohol. The final surface cleaning, just prior to deposition, was performed in the reactor chamber with oxygen plasma etching for 3 min at 40 sccm of O_2 flow rate and 300 W of RF power.

The following chemicals were applied in the deposition processes as precursor compounds:

- Sigma Aldrich 99.9% titanium (IV) chloride of a density 1.73 g/ml at 20 °C (lit.) as a source of titanium
- Sigma Aldrich 99,99% iron pentacarbonyl of a density 1.49 g/ml (liquid) as a source of iron
- Sigma Aldrich 99,99% copper (II) (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) of a density N/A (solid) as a source of copper
- Linde Gas 99,999% gaseous O_2 as a source of oxygen
- Linde Gas 99,999% gaseous Ar as a carrier gas

2.2. Deposition equipment and procedures

The RF PECVD equipment used in this work is schematically

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