Materials Research Bulletin 48 (2013) 4022–4031

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Mechanical, photocatalytic and microbiological properties of titanium dioxide thin films synthesized with the sol–gel and low temperature plasma deposition techniques

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ARTICLE INFO

Article history:
Received 10 January 2013
Received in revised form 10 June 2013
Accepted 12 June 2013
Available online 20 June 2013

Keywords:
A. Oxides
B. Sol–gel chemistry
B. Plasma deposition
D. Mechanical properties
D. Catalytic properties

ABSTRACT

In this work, selected mechanical, photocatalytic and biological properties of thin titanium dioxide films, synthesized with the sol–gel and radio frequency plasma enhanced chemical vapor deposition (RF PECVD) techniques, were compared. In both cases, austenitic stainless steel was used as a substrate, and titanium organic connections served as TiO_2 precursors. Prior to the deposition, several substrates had been surface plasma activated and the film adherence to activated and non-activated surfaces was compared.

The TiO_2 films deposited with the RF PECVD technique were characterized by better mechanical properties than those of the sol–gel coatings. The bactericidal activity of the plasma deposited films was also higher. All coatings significantly reduced the formation of bacterial biofilm. In the domain of water photowettability, similar photowetting effects were obtained for the PECVD and sol films. Finally, an important finding concerns the photocatalytic properties of amorphous TiO_2 coatings, synthesized with the RF PECVD technique.

1. Introduction

Due to their excellent physical properties such as high magnitudes of dielectric constant and refractive index [1], optical transmittance in the visible range [2] and good mechanical [3] and chemical stability [4], thin titanium dioxide (TiO_2) films attract a considerable amount of scientific interest. Their properties make them potential candidates for several new applications in such areas of technology as photocatalysis [5], sensors [6], solar cells [7], optical filters [8,9] and protective coatings [2].

The question of water wettability of a solid surface is vital from the point of view of a number of commercial applications. Studying surface modification procedures leading to super-hydrophobic (water contact angle higher than 150°) or super-hydrophilic surfaces (water contact angle lower than 5°) has attracted a great deal of attention [10]. A super-hydrophilic surface is particularly useful in those applications that involve, among others, self-cleaning antifogging or antifouling functions of a material. As far as titanium dioxide is concerned, it becomes super-hydrophilic after its illumination with light of a wavelength depending on the material crystalline structure [11]. Structurally, TiO_2 has polymorphic properties characterized by the existence of three crystalline phases, namely rutile, anatase and the least stable brookite. Rutile is a high temperature phase and has a refractive index of about 2.6, while anatase is formed at lower temperatures and has a refractive index of 2.3 [12].

Rapid technological progress and the advance of civilization related diseases stimulate an ever growing demand for biomaterials. This demand is principally due to a larger amount of injuries resulting from such factors as diet related anomalies of the osseous system and a growing number of traffic accidents. Over eighty thousand femoral joint endoprostheses are implanted each year in Western Europe alone. Materials used to manufacture implants comprise metals, ceramics, glasses, polymers, multilayered and composite materials, coatings, including all kinds of carboneous materials [13,14]. However, due to their advantageous mechanical properties, metallic biomaterials still remain irreplaceable in numerous medical applications.

Significant problems concerning biomaterials are connected with bacterial cell adhesion and biofilm formation. The adhesion of bacteria, which begins with the adsorption of proteins on the biomaterial surface, makes the first step towards development of the so called bacterial biofilm on that surface. Its formation on the surface of an implant, often leading to endosystemic infections,

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http://dx.doi.org/10.1016/j.materresbull.2013.06.024

may be fairly dangerous [15]. This is the reason why proper surface preparation of a material designed for contact with a living tissue constitutes one of the principal engineering challenges of biomaterials. Today, one of the most broadly used solutions comprises coating the material surface with ceramic TiO_2 films [16]. This imposes a necessity to obtain a durable connection between the metallic substrate and the ceramic coating, which renders it necessary to control mechanical properties such as hardness and interface adherence of the TiO_2 films [17]. It is commonly known, in general, that the properties of coatings strongly depend on the method of their manufacturing.

Thin TiO_2 films can be prepared by a variety of deposition techniques, such as the sol–gel processes [18], chemical vapour deposition [19], reactive evaporation [20,21], various reactive sputtering techniques [1,22], ion beam assisted processes [23], atomic layer deposition [24] pulse laser deposition [25] and plasma enhanced chemical vapor deposition [8,9,26,27] or hybrid techniques as plasma enhanced aerosol–gel method [28].

The principal aim of the present work was to investigate the effect of deposition method of thin titanium dioxide films on their morphology and properties. For the sake of a comparison, two deposition techniques were selected: the sol–gel technique and the radio frequency plasma enhanced chemical vapor deposition (RF PECVD) method. Selection of the former is due to the fact that it is a simple technique, broadly used to manufacture commercial TiO_2 films, while their synthesis using the latter method is in a phase of advancement with its principal use in the area of thin film interference filters [8,9], and also more and more frequently attempted photocatalytic applications [26,27]. From both a viewpoint of equipment infrastructure and of the physical chemistry of film formation, the RF PECVD technique is a more complex method. However, there are a number of advantages which signify its specific position among other thin film synthesis methods – it is characterized by relative simplicity of the process control, combined with high quality of the resulting coatings [29]. Their mechanical properties, such as hardness or adhesion for instance, are claimed to be much better than those of the sol–gel coatings. However, it is usually hard to verify such claims because only few publications exist in the literature which directly compare the properties of sol–gel synthesized films to those obtained by other methods [30–32]. In their work, Guillard et al. present a comparison of the thickness, particle size and porosity of the films obtained with the sol–gel and RF PCVD techniques and evaluate their optical and photocatalytic properties in terms of how they affect the reaction rate of the oxidative degradation of butanol–dioic acid [32].

In the present work, morphology, roughness, mechanical properties, photowettability, photocatalytical and biological properties of TiO_2 coatings, prepared on medical steel substrates with the sol–gel technique, are compared to the properties of RF PECVD films deposited on identical substrates. Two homological metalorganic TiO_2 precursors have been used in the work: titanium (IV) butoxide in the sol–gel method and titanium (IV) ethoxide in the RF PECVD technique. Selection of the precursors was carefully considered and resulted from long years experience in the synthesis of TiO_2 films with both methods. Titanium (IV) butoxide was selected for the sol–gel deposition because of its satisfactory stability and resisitivity to the effect of atmospheric moisture. In the RF PECVD technique, on the other hand, a criterion was the ease of precursor evaporation and vapor transport. Titanium (IV) ethoxide has a lower boiling point and is characterized by higher vapor pressure, therefore faciliating its input procedures. In the case of homological metalorganic precursors, while affecting the yield of deposition (the shorter chain, the higher yield) the number of carbon atoms in the aliphatic chain should not significantly affect the properties of the films deposited [33].

2. Experimental

2.1. Materials

Medical implant quality SANDVIK BIOLINE stainless steel 316LVM (ISO 5832-1) was used to produce substrates in the form of 5 mm high pellets of 16 mm in diameter. Prior to depositions their surface was polished with Struers DiaPro Plus3 diamond paste of a grain size of 3 μm. The substrates were washed for 15 min in an ultrasonic bath filled with methyl alcohol, and then dried with a stream of air. For an assessment of adhesion, the samples were divided into three series. In the first series of samples, the coatings were deposited onto substrates directly after their cleaning. In the second series of samples, prior to their deposition, the substrate surfaces were subjected to nonreactive RF plasma processing in argon discharge at the following parameters: flow rate of argon F_{Ar} = 400 sccm, discharge power W = 300 W and discharge duration t = 3 min. Finally, in the third series, the surfaces were subjected to the reactive RF plasma processing in oxygen using the following parameters: flow rate of oxygen $F_{O_2} = 400$ sccm, discharge power W = 300 W and discharge duration t = 3 min. Identical procedures of substrate surface preparation were used prior to both deposition processes.

In one exemption, namely in the case of XRD analyses, stainless steel substrates were replaced with silicon wafer substrates of (1 1 1) orientation and dimensions 7 mm × 20 mm × 1.5 mm.

In the sol–gel method, 97% purity titanium (IV) butoxide, manufactured by Sigma–Aldrich, was used as the coating precursor, while technical grade titanium (IV) ethoxide, also manufactured by Sigma–Aldich, served as the precursor in the PECVD technique. Linde Gas technical grade gaseous oxygen was used as the oxygen source.

2.2. Thin film synthesis

2.2.1. Sol–gel method

For the synthesis of coatings with the sol–gel method, a sol prepared with titanium(IV) butoxide (TBT) precursor was used. In order to get the sol ready, the precursor was first dissolved in anhydrous ethyl alcohol (C_2H_5OH). To this solution, a solution of acetic acid in water was added at the following molar proportions: TBT: H_2O: CH_3COOH: C_2H_5OH) = 1:10:1:60. Concentration of the Ti precursor in the final solution (sol) amounted to 0,25 mol/dm^3 while its pH (measured using Hanna Instruments HI221 Ph-metre equipped with an electrode for anhydrous liquids) equalled 4.7.

The coatings were produced with a dip-coating technique. The substrates were dipped in the sol and then removed from that sol at the rate of 60 mm/min.

Following the deposition, samples were dried for 15 min at room temperature and then heated in the oven for another 15 min at 500 °C. The cycle deposition/drying/thermal treatment was repeated three times. A schematic representation of the sol–gel deposition procedure is shown in Fig. 1A.

2.2.2. RF PECVD method

A schematic view of the RF PECVD equipment is presented in Fig. 1B. One of the major elements of that equipment is the RF Power Products, model RF5S power generator, working at the frequency of 13.56 MHz in the power range of 0–500 W with frequency accuracy of ±0.01%. In the present work, the coatings were deposited at power levels of 100 W, 200 W and 300 W. The energy generated was directed to the deposition chamber through an impedance matching circuit, with the substrates placed on the lower, RF powered electrode. The reactor was equipped with a working gas (vapours of metalorganic precursor–titanium (IV) ethoxide $Ti(OC_2H_5)_4$ plus gaseous oxygen) supply line. The flow rate of