



Fluorine doped titanium dioxide films manufactured with the help of plasma enhanced chemical vapor deposition technique

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ABSTRACT

In this work, a manufacture of TiO₂ coatings doped with fluorine, in a concentration range of 0.6 to 6.7 at.%, is presented. The coatings were deposited onto silicon and quartz substrates with the help of radio frequency plasma enhanced chemical vapor deposition technique. They were characterized with regard to their elemental composition, chemical structure, phase composition, surface topography, optical properties, photo-wettability and bactericidal properties. For that purpose, such analytical techniques as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, grazing incidence X-ray diffraction (GIXRD), scanning electron microscopy, atomic force microscopy, ultraviolet–visible absorption spectroscopy and variable angle spectroscopic ellipsometry were used.

GIXRD analysis of the coatings doped with fluorine shows their amorphous structure. Apart from TiO₂ bonding, FTIR and XPS analyses of the films reveal a presence of Ti–F and O–F bonds. Surface morphology studies indicate an increasing number of surface defects along with growing fluorine content. The coatings exhibit promising optical properties with some of them showing a super-hydrophilic effect as well. On the other hand, the bactericidal effect of fluorine doped TiO₂ coatings is weaker than that of plain TiO₂.

1. Introduction

Due to its potential to oxidize a broad range of chemicals, both organic and inorganic, titanium dioxide (TiO₂) is one of the most frequently used photocatalysts, also in a nanometer scale. In addition, it is characterized by a high bactericidal activity in contact with numerous bacterial lines [1–3]. TiO₂ surface has also a well-recognized self-cleaning potential resulting from this compound ability to form super-hydrophilic surfaces under the effect of ultraviolet (UV) radiation [4]. Unfortunately, high reactivity of its stable polymorphic form of anatase is observed for TiO₂ illuminated with UV of a wavelength lower than 390 nm, which corresponds to the optical gap value of 3.3 eV [1,2,5]. A high-temperature crystalline form of titanium dioxide, known as rutile is characterized by the optical gap value of 3.1 eV, which corresponds to the excitation threshold wavelength of 410 nm [6]. In order to shift this threshold towards visible light, to enhance intensity of the photocatalytic process and to extend its duration after suspending illumination, different modification procedures have been proposed. One of the most commonly used method is doping TiO₂ with such minority metals

as silver [7], copper [8], iron [9], zinc [10], platinum [11] and niobium [12]. Other dopants comprise non-metallic elements, namely nitrogen [13], sulphur [14], carbon [15], boron [16], fluorine [17,18], phosphorus [19] and iodine [20]. In addition, such additives as oxides [21], sulphides [22] as well as titanium at the oxidation level of +3 [23] may be also introduced.

As discussed above, the mechanism of photocatalysis requires an absorption of a quantum of radiative energy of a minimum magnitude exceeding the optical gap threshold value. An electron transfer from the valence band to the conduction band then takes place with a formation of an electron-hole pair. Such an excited couple may either recombine immediately or it may be transformed into a metastable state, in which it reacts with water and oxygen molecules with the formation of reactive forms of oxygen [1,24].

As far as doping with non-metallic elements is concerned, there are three excitation mechanisms discussed in the literature: a band gap narrowing mechanism proposed by Morikawa et al. [24], an impurity energy levels mechanism presented by Irie et al. [25] and an oxygen vacancies mechanism described by Ihara et al. [26]. In 2001, Asahi

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et al. [27] conducted theoretical calculations of electron density distribution in a doped anatase crystal. The calculations were performed for TiO₂ materials in which oxygen was substituted with fluorine, nitrogen, carbon, sulphur and phosphorus. In addition, a system was analyzed in which nitrogen atoms had been incorporated in an interstitial way, either entirely or partly [27]. Their calculations point to a narrowing of the catalyst forbidden band that results from mixing titanium dioxide O 2p level with electron states of the dopants. As a consequence, a shift of absorption characteristics towards higher wavelengths is observed. Due to a lower ion radius of the dopant, a substitution of oxygen with nitrogen requires less energy. On the other hand, a modification of titanium dioxide with carbon and phosphorus results in a formation of extra forbidden bands, outside of this compound's forbidden band. Finally, doping with iodine induces a dipole moment facilitating separation of excited charge carriers [28].

Intensive studies on TiO₂ coatings doped with non-metallic additives are now underway and they include fluorine doping. According to the literature, doping of titanium dioxide nanoparticles with fluorine increases their photocatalytic activity [17,18,29]. Hattori et al. have shown that this effect is due to the extension of electron-hole photo-generation time [30]. Doping may also lead to a reduction of Ti⁴⁺ to Ti³⁺ ions through a charge compensation mechanism. A presence of Ti³⁺ ions, on the other hand, may lower the rate of electron-hole recombination, thus leading to an increase of photocatalytic activity [31]. An enhancement of photocatalytic activity should take place because of a production of OH* radicals, formed thanks to a presence of Ti–F bonds. Later, in 2002, Yu et al. reported doping titanium dioxide with fluorine introduced directly to the TiO₂ matrix [32]. Li et al., in turn, described a way to dope TiO₂ with fluorine by means of spray pyrolysis technique [17]. In his work of 2012, Lin has shown that an admixture of silver and fluorine to TiO₂ coatings deposited with the sol-gel technique substantially enhances their photoactivity in both UV and visible ranges of radiation [33]. Finally, Dozzi et al. in 2013 described a potential to increase, by means of fluorine doping, electron-hole recombination times in a sol-gel type of coatings [34].

In the present work, fluorine doped titanium dioxide coatings manufactured with the help of radio frequency plasma enhanced chemical vapor deposition (RF PECVD) technique are described. As a fluorine precursor, liquid pentafluoropropionic acid has been used. The coatings, containing fluorine in a range of approximately 0.6 at.% to ca. 6.7 at.%, were subjected to a throughout examination in terms of their elemental and phase composition, chemical bonding, morphology and surface topography. In order to assess their optical properties, such as index of refraction, extinction coefficient and optical gap, the films were investigated by means of variable angle spectroscopic ellipsometry (VASE) and ultraviolet-visible (UV–Vis) absorption spectroscopy. Water wettability of the coatings was measured as a function of UV illumination time, with the excitation durability following their storage in the darkroom being recorded as well. Finally, bactericidal properties of the films illuminated with the UV light were also assessed.

2. Experimental

2.1. Materials

For UV–Vis spectrophotometric measurements, the coatings were deposited onto 18 × 18 cm quartz substrates of a thickness equal 0.25 mm. In all remaining cases, (111) silicon wafers polished on both sides and having resistivity between 0.005 and 0.02 Ω·cm, thickness equal 500 ± 25 μm, and surface area of approximately 1 cm², were used as substrates.

The following chemicals were used as process precursors:

- Sigma Aldrich titanium (IV) chloride (TiCl₄) of 99.9% purity and density of 1.73 g/mL at 20 °C as a source of titanium
- Linde Gas oxygen of 99,999% purity as a source of oxygen

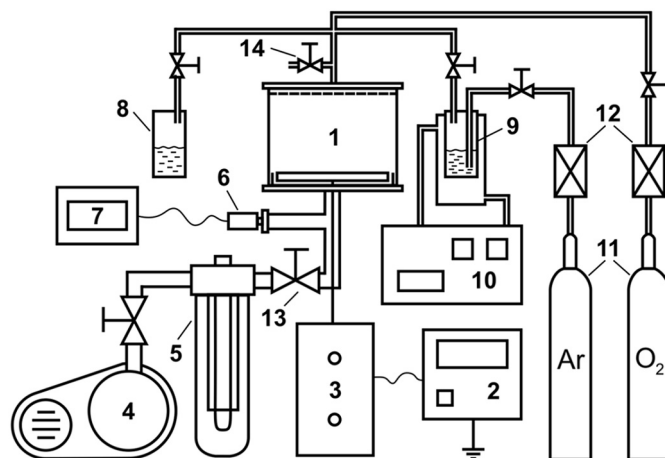


Fig. 1. RF PECVD reactor used for the synthesis of both plain and fluorine doped TiO₂ coatings: 1 — deposition chamber, 2 — RF generator, 3 — matching circuit, 4 — vacuum pump, 5 — cold trap, 6 — pressure gauge, 7 — pressure readout, 8 — fluorine source precursor container, 9 — titanium source precursor container, 10 — precursor temperature control system, 11 — gas cylinders, 12 — flow controllers, 13 — main vacuum valve, 14 — venting valve.

- Sigma Aldrich pentafluoropropionic acid of 97% purity and density of 1.561 g/mL at 20 °C as a source of fluorine
- Linde Gas argon of 99.999% purity as a carrier gas

2.2. Deposition procedure

The RF PECVD equipment applied for the deposition of fluorine doped TiO₂ coatings is presented in Fig. 1. The central part of this equipment is comprised of a deposition reactor, consisting of two parallel stainless steel electrodes separated from one another with a 20 cm high glass cylinder. The lower electrode is supplied with energy from an RF Power model RF 5S power generator coupled with an impedance matching network. Working frequency equals 13.56 MHz. A more detailed description of this equipment is given in Reference [35].

For the purpose of film deposition, titanium precursor was held in a bubbler maintained at 0 °C, with argon carrier gas being forced through this bubbler at the flow rate of 1.5 cm³/min. As titanium oxidizing medium, gaseous O₂ was used and it was supplied directly to the reactor at the flow rate of 50 cm³/min. Fluorine precursor, liquid pentafluoropropionic acid was supplied from a container maintained at 25 °C. This, together with a precise control of its evaporation rate with a needle control valve allowed one to obtain a volume content figures of its vapor of 0.18, 0.41, 0.65, 0.94 and 1.25%, respectively.

All the deposition processes were performed at the RF power of 300 W and initial pressure of 1 Pa, with the process duration amounting to 40 min.

2.3. Films characterizations

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 300 μm × 700 μm, with technical details of the analysis being given elsewhere [35]. Evaluation of XPS data was conducted with the help of a Kratos Vision 2 software. Shirley algorithm was applied for the purpose of background subtraction and the adventitious carbon main peak (C 1s, 284.8 eV) was used for each spectrum final calibration.

Grazing incidence X-ray diffraction (GIXRD) studies were carried out in order to determine phase composition of the coatings. An Empryan Panalytical XRD diffractometer, working with Cu Kα radiation (λ = 0.15418 nm) was used for that purpose. The measurements

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