



Plasma enhanced chemical vapor deposition of iron doped thin dioxide films, their structure and photowetting effect



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ABSTRACT

Radio frequency plasma enhanced chemical vapor deposition (RF PECVD) technique was applied for the purpose of deposition of iron doped titanium dioxide coatings from a gaseous mixture of oxygen with titanium (IV) chloride and iron (0) pentacarbonyl. Glass slides and silicon wafers were used as substrates. The coatings morphology was investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Their elemental and chemical composition was studied with the help of X-ray energy dispersive spectroscopy (EDS) and Fourier transform infrared (FTIR) spectroscopy, respectively, while their phase composition was analyzed with the Raman spectroscopy. For the determination of the film optical properties, ultraviolet (UV–Vis) spectroscopy techniques were used. Iron content in the range of 0.07 to 11.5 at.% was found in the coatings. FTIR studies showed that iron was built-in in the structure of TiO₂ matrix. Surface roughness, assessed with the SEM and AFM techniques, increases with an increasing content of this element. Trace amounts of iron resulted in a lowering of an absorption threshold of the films and their optical gap, but the tendency was reversed for high concentrations of that element. The effect of iron doping on UV photowettability of the films was also studied and, for coatings containing up to 5% of iron, it was stronger than that exhibited by pure TiO₂.

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1. Introduction

Thin titanium dioxide films are known to exhibit photocatalytic activity, consisting in a considerable alteration of their surface chemistry following an exposure to UV light [1]. That activity is manifested, among others, by an occurrence of a strong disinfecting effect induced by an illumination [2]. However, it is not easy to effectively utilize it in commercial applications because of a high magnitude of the optical gap, amounting to 3.2 eV. Its consequence is a fact that it is only after illumination with the UV light of a wavelength lower than 380 nm, that the photocatalytic properties of TiO₂ coatings can be activated [3]. This presents a serious application obstacle, since the above range constitutes approximately 5% of the full spectrum of the solar radiation only [4,5]. An additional difficulty results from a very low, of an order of magnitude of nanoseconds, recombination time of the (e[−], h⁺) pair, which impedes the course of redox reactions taking place on the material surface. In order to increase recombination time and to shift the absorption threshold of titanium dioxide in the direction of visible range,

attempts of its doping with such elements as transition metals (Fe, Cr, Co, V, Mo, Ru or Re) [6–9] or non-metals (N, S, C, I, P, F and B) [5,9,10] are often undertaken. Due to a formation of “shallow electron or hole traps” in its structure [11], a trace admixture of transition metals in a TiO₂ film substantially extends electron–hole recombination time and increases its photocatalytic efficiency. In addition, the doping may affect optical properties of the film. Among all transition metals, one of the best comprehended and the most effective dopants of titanium dioxide coatings is iron (III), of a cation radius equal 0.64 Å, very close to that of titanium (IV), amounting to 0.68 Å [12]. Thanks to that similarity, iron atoms easily replace titanium in the crystalline TiO₂ network. In addition, the energy level of the Fe³⁺/Fe²⁺ couple is slightly higher than the TiO₂ valence band edge, and that of the Fe⁴⁺/Fe³⁺ couple is slightly higher than the TiO₂ conduction band edge [11,13]. These advantageous energetic states of iron ions allow them to form effective traps for holes and electrons, substantially extending their recombination time. The magnitude of an optical gap of α-Fe₂O₃ amounts to 2.2 eV [14]. Therefore, an iron addition to a TiO₂ film should result in lowering optical gap of the latter, thus shifting its excitation wavelength in the direction of visible light. The results of electrical and optical studies on titanium dioxide, both undoped and doped, confirm their potential application as highly effective coatings for solar cells which, at the same time, exhibit self-cleaning properties [15,16]. These properties originate from the

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photowetting effect exhibited by titanium dioxide and consisting in a surface transition from hydrophobic to strongly hydrophilic following its illumination. The final water wetting angle may even attain values lower than 5° , which in the literature is referred to as super-hydrophilicity [17]. Titanium dioxide has also good optical properties such as high refractive index, low extinction coefficient [18].

The properties of any material to a large extent result from its broadly understood structure, including crystalline lattice, grain size and shape, surface morphology etc. These parameters, on the other hand, strongly depend on a method of manufacture. Doped TiO_2 coatings may be deposited with various methods of which, due to its simplicity, the sol–gel method is the most abundant one [19]. In the present work a different technique, namely a radio frequency plasma enhanced chemical vapor deposition (RF PECVD) has been applied in order to synthesize thin TiO_2 films doped with iron. For that purpose, TiCl_4 was used as a source of titanium, gaseous O_2 as a source of oxygen, and $\text{Fe}(\text{CO})_5$ as a source of iron. The coatings were investigated with respect to their elemental composition, chemical bonding, phase composition and optical properties, photowetting as well as their surface morphology and roughness.

2. Experimental details

2.1. Materials

The Fe– TiO_2 coatings were synthesized on the following substrates:

- One side polished silicon wafers of a $\langle 100 \rangle$ orientation, 1 cm^2 surface area and 0.7 mm thickness were used in SEM/EDS and AFM studies of the coatings as well as in their FTIR, Raman and photowetting tests.
- Microscope glass slides of the $10 \times 10 \times 0.1 \text{ mm}$ dimensions were used in optical characterization of the films with the help of UV–Vis spectroscopy.

Materials used in the RF PECVD process comprised: TiCl_4 (Sigma-Aldrich, high grade purity) of density at 20°C equal 1.73 g/cm^3 , used as a source of titanium, and gaseous oxygen (Linde Gas, purity 99,999), used as a source of oxygen. As a source of iron, Sigma-Aldrich $\text{Fe}(\text{CO})_5$ of a 99.99% purity and density at 20°C equal 1.49 ml/g was applied. In addition, argon (Linde Gas, purity 99,999) was used as a carrier gas for the TiCl_4 vapors.

2.2. Deposition process

The RF PECVD equipment, used for the deposition of iron doped titanium dioxide coatings consists of three basic subunits:

- Deposition chamber equipped with a system supplying working gases and deposition precursors
- Radio frequency generator with matching circuit
- Vacuum system.

In this equipment, low temperature plasma is generated. The deposition chamber is built of two electrodes, the upper grounded electrode and the lower RF powered electrode, which are separated with a ring of glass. The RF electromagnetic field of a frequency of 13.56 MHz field is applied to the lower electrode from the RF Power Product model RF 5S generator through a self-designed matching circuit. The upper, grounded electrode serves also as a shower for a supply and even distribution of working gases and deposition precursors. Both electrodes have the same dimensions, with their diameter amounting to 200 mm, but the lower electrode is shielded with a grounded shield of a larger surface area. In the gas supply system, inputs of oxygen and argon inputs are controlled with the help of MKS Baratron model 1179A mass flow controllers. Both liquid precursors, i.e. TiCl_4 and

$\text{Fe}(\text{CO})_5$, are supplied to the chamber in a form of vapors, delivered from respective bubblers. The titanium chloride input is controlled by the bubbler temperature and by the flow rate of the bubbling argon, while the flow rate of evaporated $\text{Fe}(\text{CO})_5$ is regulated with a system of needle valves, affecting its vapor pressure above the mirror of the liquid. The operational parameters of the deposition of Fe doped TiO_2 films in the described equipment are given in Table 1.

2.3. Film diagnostics

In order to evaluate large area surface morphology of the coatings, a Carl Zeiss ULTRAPlus scanning electron microscope (SEM), supported with the SmartSEM software, was used. The microscope is equipped with a FEG type cathode, which allows one to conduct observations at low accelerating voltage in the range of 0.5–30 kV. In order to dissipate the surface charge collected at the specimen surface, a Carl Zeiss Charge Compensator mechanism was used. This mechanism enables an observation of samples of poor electrical conductivity as well as that of non-conductive samples. For scanning the Fe/ TiO_2 specimens, an accelerating voltage of 2.5 kV and a distance of approximately 6 mm were applied. Under such experimental conditions it is crucial that the samples are not modified in any way.

For an analysis of the chemical composition of the films, an Oxford Instruments X-Max20 EDS detector was used. For that purpose, the accelerating voltage of the microscope was set at 10 kV with the working distance being 6.5 mm. The chemical composition was analyzed with the help of the Charge Compensator without any prior surface treatment of the samples.

To evaluate the quality of sample's surface, a JPK NanoWizard III atomic force microscope, working in a contactless mode, was used. The microscope was equipped with a Nanosensors type CPPP-NCHAuD-50th cantilever. Samples were scanned in the original form without any modification. The area scanned was $10 \times 10 \mu\text{m}$. The data acquired were subsequently evaluated using JPK DataProcessing v4.3.50 software.

Raman spectra were acquired at 20°C with the help of JobinYvon T64000 triple-gratings Raman spectrometer equipped with the Olympus BX40 confocal microscope. Argon ion laser line ($\lambda = 514.5 \text{ nm}$) was used for sample excitation, whereas the acquisition time was adjusted for each sample independently in order to obtain a satisfactory signal/noise ratio.

FTIR analyses were performed within the range of 4000 cm^{-1} to 400 cm^{-1} , with the resolution of 2 cm^{-1} , using a Nicolet model iS50 FTIR spectrometer. The measurements were carried out in a transmission mode, using absorbance as the parameter recorded. A single measurement was comprised of 120 scans.

For recording transmission characteristics in the wavelength range of 250 to 1000 nm, UV–Vis absorption spectroscopy was used, with the Thermo Scientific model Evolution 220 UV–Vis spectrometer applied for the purpose. The transmission data were later used for the determination of the optical gap of the films. The optical energy band

Table 1
Deposition parameters of thin TiO_2 coatings doped with iron.

Glow discharge power	300 W
Deposition time	45 min
Oxygen etching time	2 min
Oxygen flow	50 sccm
Volume content of iron pentacarbonyl in the gas phase	0.12, 0.18, 0.36, 0.48, 0.66, 0.90, 1.5%
Argon flow	1–2 sccm
Temperature of liquid TiCl_4	0°C
Temperature of liquid $\text{Fe}(\text{CO})_5$	25°C
Output pressure	8 mTorr

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