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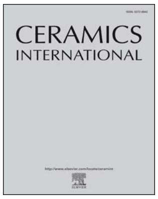

Morphology, structure and photowettability of TiO_2 coatings doped with copper and fluorine

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ABSTRACT

The work reports synthesis, structure and properties of doubly doped titanium dioxide coatings activated by ultraviolet and visible light. Copper within a concentration range of 0.4–3.4 at% and fluorine within a concentration range of 1.7–9.4 at% were introduced as dopants. The coatings were prepared with the help of radiofrequency plasma enhanced chemical vapor deposition technique with a single precursor compound providing both dopants and titanium (IV) chloride being a source of titanium. Elemental composition and chemical bonding analyses of the coatings were carried out with the help of X-ray photoelectron spectroscopy. The results indicate that both admixtures are chemically bound to the TiO_2 matrix – a notion confirmed by Fourier transform infrared spectroscopy. Phase composition studies, performed with a low angle X-ray diffraction method, revealed a presence of a threshold concentration of the dopants affecting the coatings crystallinity. Surface morphology and its topography were studied with the help of scanning electron microscopy and atomic force microscopy. Several coatings exhibited a superhydrophilic effect upon relatively short time of illumination.

1. Introduction

Certain semiconducting materials exhibit photocatalytic activity resulting from their receptivity to excitation upon an impact of energetic photons, able to move electrons from valence band to conduction band, thus creating electron-hole pairs [1,2]. Under such conditions, active forms of oxygen, capable of an oxidation of both inorganic [3] and organic compounds in air [4], water [5] and on the solid surfaces [6], are generated at the semiconductor surface. They also inflict destructive effects on bacteria [7], fungi and molds [8].

A semiconductor of such characteristics is titanium dioxide [4–9], a material frequently used in environment protection and health care applications [10]. A disadvantage of using bare TiO_2 in these applications is the fact that it can only become excited by the UV radiation [7–9]. This is a reason why structural modifications able to shift the excitation threshold towards visible light are being developed. In addition to threshold shifting, such modifications may also intensify excitation effect by extending charge carrier recombination times [11]. For that purpose, admixtures of either metallic or non-metallic elements are introduced into semiconductor structure. This brings about overlapping of “p” orbitals which boosts charge transport towards TiO_2 surface and leads to an enhancement of photocatalytic activity [12].

One of the most frequently used, both in photovoltaic and in photocatalytic applications, metallic TiO_2 dopants is copper [13]. The fact that the absorption range of both copper oxides overlaps with the scope of visible part of solar radiation makes them serious candidates for creating heterostructures with TiO_2 [14]. Both copper (I) and copper (II) oxides are characterized by “p” type conduction [15] with their optical gap values amounting to 2.0–2.2 eV and to 1.2–1.5 eV, respectively [16]. Since the magnitude of optical gap determines absorption threshold, copper oxides absorb a broad range of visible light [17]. This is a reason why copper is frequently used to manufacture nanocomposites with titanium dioxide for photocatalytic applications. It has been demonstrated that such systems are characterized by high oxidative power towards phenol [18], 4-chlorophenol [19], methylene blue [20] or rhodamine B [21]. They are also employed to destroy certain bacterial strains such as *Escherichia coli*, for instance [22].

As far as non-metallic dopants of titanium dioxide are concerned, nitrogen is the most frequently used one. It is assumed that doping TiO_2 with N atoms leads to a formation of an intermediate energetic level that results from mixing N 2p and O 2p orbitals [23]. Similar is titanium dioxide behavior when doped with other non-metals, including fluorine

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[24].

Recently, a so called "double doping" either with metal-metal or with metal-nonmetal systems is reported in a number of publications [25–32]. Combining dopant materials of different properties may lead to a synergy effect with a shift of the absorption threshold towards visible light and an extension of the excited state life time [26]. Among others, such combinations as Pd/Cu TiO_2 [27], Au/Cu TiO_2 [28], N/Cu TiO_2 [29], Cu/C TiO_2 [30], Cu/S TiO_2 [31] are used for that purpose. In 2016, a work was published by N.S. Leyland et al. [32] wherein the authors reported doping sol-gel titanium dioxide coatings simultaneously with fluorine and copper. When illuminated with visible light, the resulting photoactive material was characterized by a high bactericidal effect in contact with the *Staphylococcus aureus* strain.

It is important to remember that an appropriate selection of dopant materials, although essential, does not constitute a condition sufficient for a synthesis of highly efficient photoactive substance. Equally important are the form, oxidation degree and concentration of the dopants as well as the form of the TiO_2 matrix itself [33]. For example, titanium dioxide samples doped with the same minority element at the same concentration will still exhibit different photocatalytic activity depending on whether the matrix has a form of a powder or a thin film [34].

In the present work, a radio frequency plasma enhanced chemical vapor deposition (RF PECVD) method is applied for the purpose of depositing TiO_2 coatings doubly doped with copper and fluorine. This technique is rather rarely used for such applications [35,36]. However, with an appropriate selection of the precursor compound it offers a possibility of a simultaneous doping of the matrix with two or more elements. The work reports doping the TiO_2 coatings with copper and fluorine from a single source such as copper (II) (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate). The resulting coatings have been characterized with regard to their surface morphology, elemental composition, chemical bonding, optical properties and photowettability.

2. Experimental

2.1. Materials

2.1.1. Chemicals

Chemical compounds applied in this work as source materials comprise:

- a source of titanium – 99.9% titanium (IV) chloride of Sigma Aldrich
- a source of oxygen – 99,999% gaseous O_2 of Linde Gas
- a source of copper and fluorine – 99,99% copper (II) (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) of Sigma Aldrich

Apart from that, 99,999% gaseous argon of Linde Gas was used as a carrier gas.

2.1.2. Substrates

The following materials were used as substrates:

- quartz slides of dimensions of 18 × 18 mm and a thickness equal 0.25 mm for UV–Vis absorption measurements
- (111) silicone wafers of a thickness equal 500 ± 25 μm for other measurements

2.2. Deposition process

The coatings were produced by means of the RF PECVD technique using a parallel plate reactor, whose schematic representation is shown in Fig. 1. A very detailed description of that reactor has been given by Sobczyk-Guzenda et al. in Ref. [35].

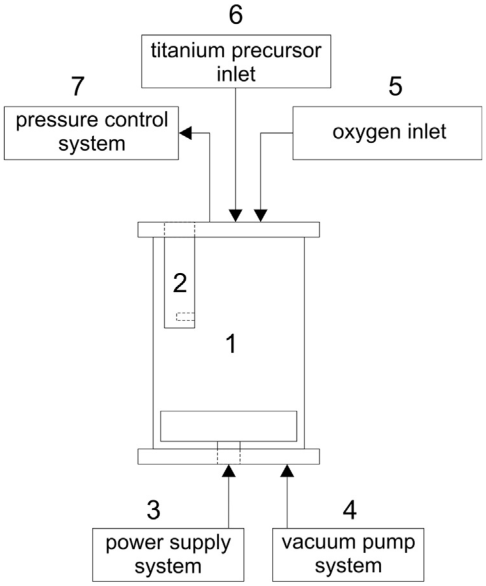

Fig. 1. Schematic view of the equipment for the synthesis of copper and fluorine doped TiO_2 thin films: reaction chamber (1), temperature controlled sublimator used to evaporate the solid-state precursor of copper and fluorine (2), RF power supply system (3), vacuum pump system (4), oxygen inlet (5), titanium precursor inlet (6), and pressure control system (7).

In a process of titanium dioxide deposition, the source of titanium was comprised of liquid titanium (IV) chloride $TiCl_4$, evaporated in a bubbler maintained at 5 °C and carried by argon carrier gas flowing at 1.5 sccm. Both dopants, copper and fluorine, were introduced using a single precursor, namely copper (II) (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) supplied from a sublimator placed directly inside the deposition chamber. The sublimator was resistance heated and its temperature, controlled with a thermocouple and a switch, amounted to 60 °C, 70 °C, 80 °C, 90 °C and 100 °C, which corresponded to $1.5 \cdot 10^{-5}$, $2 \cdot 10^{-5}$, $2.4 \cdot 10^{-5}$, $2.7 \cdot 10^{-5}$ and $3 \cdot 10^{-5}$ mole of the evaporated precursor for a single process, respectively.

With a separate gas supply line, oxygen was introduced into the reactor at the flow rate of 50 sccm. Both oxygen and argon flow rates were controlled with the help of MKS Baratron 1179A mass flow controllers. RF power of deposition and the system initial pressure were kept constant and they amounted to 300 W and 8 mTorr, respectively. Deposition time was equal 30 min. Each deposition process was preceded by reactive ion etching of the substrates with oxygen, carried out for 3 min at the oxygen flow rate of 50 sccm and the glow discharge power of 300 W.

2.3. Characterization of the films

The XPS analysis of the coatings was performed with a Kratos AXIS Ultra XPS spectrometer. For that purpose, an Al Kα X-ray source of an excitation energy of 1486.6 eV was used. The area of data collection was 300 μm × 700 μm, with the anode power amounting to 150 W. The hemispherical electron energy analyzer was operating at a pass energy of 20 eV and all data were collected with the use of a charge neutralizer. In order to enhance the signal-to-noise-ratio, each sample was scanned ten times. For the evaluation of XPS data, Kratos Vision 2 software was used. Shirley algorithm was applied for background subtraction and the adventitious carbon peak (C 1s, 284.8 eV) was used to calibrate each spectrum. On several occasions, argon ion beam etching of the samples was performed in order to carry out their in-depth analyses. Each etching lasted 30 s, with the beam energy equal 2 keV and the raster size equal 3 × 3 mm.

In order to determine phase composition of the coatings as well as to assess their coherent domain size, X-ray diffraction (XRD) measurements were performed. For that purpose, Empyrean Panalytical XRD