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Functional nano-textured titania-coatings with self-cleaning and antireflective properties for photovoltaic surfaces

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Abstract

Photoactive TiO_2-only transparent coatings having self-cleaning and antireflection (AR) properties were prepared by forming first a nanosol through controlled hydrolysis of tetraisopropyl orthotitanate (TIPT), followed by deposition of this nanosol on glass substrates by dip-coating with a final calcination step to form the surface nano-textured thin film. The samples were characterized in terms of nano-structure and -texture by X-ray diffraction, UV–vis spectroscopy, scanning electron microscopy and atomic force microscopy, while AR properties were investigated by transmittance measurements. Self-cleaning properties were analyzed by measuring the changes of water contact angle, and by photocatalytic degradation of a dye. The aim was to analyze how to prepare these materials and the relation of the properties of titania with the surface nano-texture, particularly in relation to obtain the properties required to their use as functional coatings for PV cells. Films with good optical characteristics and high transmittance (<1% loss in transmittance) can be obtained at low speed of dip-coating (6 mm/s) and high nitric acid concentration (0.5 M). Under optimized conditions, calcination at low temperature (400 °C) may already be sufficient to produce coatings with good functional properties, making the procedure compatible with the use of some flexible substrates. A preliminary mechanism of formation of the surface nano-texturing is also proposed.

Keywords: Titanium dioxide; Thin film; Antireflection coatings; Self-cleaning

1. Introduction

The use of photovoltaic (PV) devices to transform directly the solar energy into electrical energy is fast wide spreading to move to a decentralized and more sustainable production of energy. However, this development is posing new problems, because the decentralized use, often on the roof of building in cities, creates the issues of (i) a quick

Abbreviations: AR, antireflective; PV, photovoltaic; TIPT, tetraisopropyl orthotitanate; AcAc, acetylacetone; RMS, mean square roughness; MO, methyl orange.

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fouling of the PV devices and (ii) the need to decrease reflective properties to improve light adsorption and especially reduce the visual impact of light reflection.

The top layer of silicon solar cells, the PV cell with wider commercial use, is a cover glass having different functions (Deubener et al., 2009): (i) reduce the high reflection coefficient of silicon to improve cell efficiency, (ii) act as a radiation barrier and optical-coupling element, and (iii) protect against debris and aggressive agents present in air. Surface fouling, particularly in cities and when limited periodic cleaning is possible, still remains an issue and an improvement of antireflection (AR) properties is also generally necessary.

AR properties could be improved by (i) creating appropriate surface profiles (texturing) or (ii) depositing an AR coating, while fouling issues can be minimized by exploiting the photo-catalytic and self-cleaning properties of a cover film (Dobrzański et al., 2012; Goetzberger and Hoffmann, 2005; Dobrzański et al., 2008a,b,c). TiO_2-based thin films are often used as cover layer for PV cells, due to titania properties of (i) high photo-reactivity (Schiavello, 1988; Pelizzetti and Sepone, 1989; Fujishima et al., 1999) and -stability, (ii) super-hydrophilic behavior during irradiation, (iii) good mechanical, chemical and thermal resistance, (iv) low toxicity and cost as well (Gronet and Truman, US Patent 0,017,567 Jan 25, 2007; Gensler et al. US Patent 8,367,579 B2 Feb 5, 2013; Fujishima et al. US Patent 6,387,844 B1 May 14, 2002). The photocatalytic properties of TiO_2 and the hydrophilic effect caused by UV irradiation are well known aspects of the surface chemistry and reactivity of titania (Yates, 2009; Long et al., 2010; Taga, 2009; Zhao et al., 2008; Fujishima and Zhang, 2006). These two aspects are related. Yates (2009) suggested that photoinduced hydrophilicity in titania is due to the photo-oxidation of a non-wetting monolayer of adsorbed hydrocarbon molecules. This monolayer of adsorbed hydrocarbon molecules is initially present over the entire surface, being in equilibrium with the gas phase hydrocarbon. When photooxidation is initiated, the adsorbed hydrocarbon will slowly decrease in the region external to the droplet edge, permitting the water droplet to wet the external surface. The hydrocarbon layer under the droplet is not photooxidized because the water bulk shields this surface from extensive exposure to O_2. Therefore, the contact angle decreases, with a change from hydrophobic-like to hydrophilic-like characteristics of TiO_2 film during UV exposure.

However, much less investigated is how to obtain multifunctional photoactive self-cleaning and AR films, which should combine various additional properties to photoreactivity and photoinduced hydrophilicity: high optical properties of transmittance, AR properties, good mechanical resistance to scratches, and good adherence to glass substrate. In addition, the method of preparation has to be low cost and easily scalable for industrial production.

The specific functional characteristics of TiO_2 are closely related to its crystal structure and morphology, which depend on many factors: manufacturing method, process conditions and final heat treatment. (Centi and Perathoner, 2009a, 2012) However, the relation of these parameters with the nano-texture of the surface is typical not analyzed (Centi and Perathoner, 2009b; Ampelli et al., 2008), although it is known that an efficient self-cleaning requires a specific surface roughness to minimize the contact angle of water drops (lotus effect) and allow the efficient removal of the deposited dust particles during raining. These characteristics should be combined to an efficient photocatalytic activity, related to semiconductor properties of titania, in order to reduce (by photo-oxidation) the accumulation of grease, hydrocarbons and other contaminants on the surface. These contaminants will not only cause a lowering of the transmittance, but also reduce the effectiveness of dust removal, with thus a synergetic effect.

AR properties are depending on the surface nano-texture aspects as well (Passalacqua et al., 2014; Blanco et al., 2015), because light scattering depends on surface roughness (Harada et al., 2013) and nano-texture (Attia et al., 2002). Optical properties of the films, including transparency, are indirectly dependent on the surface roughness. The latter is related to the way the thin film is prepared (nucleation rate, film thickness, etc.) (Harada et al., 2013). These parameters influence also the optical properties of the coating (Blanco et al., 2015). The properties and behavior of titania thin films to be used with optimal performances in photovoltaic glass surfaces may thus depend in a complex way from the preparation, which in turn influences various properties (including surface nano-texture) and related functional properties (self-cleaning and AR behavior, transparency, etc.). However, there are no specific studies concerning the relation of the above properties with the surface nano-texture of titania, particularly in relation to obtaining the multifunctional properties required to their use as functional coatings for PV cells.

Many recent papers have been published on the self-cleaning and/or AR properties of titania-based thin films coatings, for example prepared by thermal evaporation and cathodic arc plasma deposition (Bedikyan et al., 2013), spray pyrolysis deposition of WO_3–TiO_2 nanoparticle (Noh and Myong, 2014), self-assembly of a block-copolymer in combination with silica-based sol–gel chemistry and preformed TiO_2 nanocrystals (Guldin et al., 2013), chemical vapor deposition of SiO_2–TiO_2 thin films (Klobukowski et al., 2013), deposition of a polyimide–titania hybrid film prepared using nano-crystalline titania (Yen et al., 2013), RF magnetron sputtering of titania (Abdullah et al., 2013), anodization of a Ti layer deposited by sputtering technique (Manea et al., 2013), dip-coating in silica-titania colloid solutions (Zhang et al., 2013), layer-by-layer assembly of silica-titania core–shell nanoparticles and silica nanoparticles as building blocks (Li et al., 2013), dip-coating in sol solutions to prepare multilayer SiO_2, TiO_2 and SiO_2–TiO_2 hybrid thin