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Use of ion-assisted sputtering technique for producing photocatalytic titanium dioxide thin films: Influence of thermal treatments on structural and activity properties based on the decomposition of stearic acid

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ABSTRACT

Titanium dioxide thin films were deposited by the reactive ion-assisted sputtering method from titanium targets at various partial pressures and deposition parameters. The films were deposited onto substrates at temperatures ranging from room-temperature conditions to 722 K. A selection of thin films was post-deposited annealed at temperatures up to 972 K for 10 min and characterized by micro-Raman spectroscopy and scanning electron microscopy (SEM) and subsequently analysed to assess their photocatalytic activity. Micro-Raman characterization revealed that the as-deposited films had either predominant amorphous, rutile-like structures, anatase-like structures or anatase-rutile mixed structures. The thin films deposited with a high substrate temperature and with energy assistance from the ion source tended to be amorphous, while films deposited on a hot substrate without ion energy assistance tended to have a mixed crystalline phase. On subsequent annealing the amorphous films changed to a rutile structure at temperatures above 672 K, while mixed anatase-rutile films changed to predominant rutile structures only after thermal treatments above 872 K. Thus, this study has revealed an astonishing persistence of the anatase-rutile mixed phase at very high temperatures and showed the possible existence of a key transition temperature at 672 K, where it was possible to see a transformation from amorphous or mixed phase to a rutile or dominant rutile mixed phase. Photocatalytic tests were undertaken by using a novel method consisting of observing the degradation of a film of stearic acid by the thin films under artificial UV radiation. Of the films investigated those with anatase-rutile mixed phases showed the greatest photoactivity. This work was essential in the understanding of the correlation between growth deposition conditions, phase transitions and photocatalytic activity. This set of experiments demonstrated that titania made under a highly oxidizing atmosphere, with no temperature applied on the substrate during fabrication and using an ion sputtering method, is a useful and valuable novel method for creating active TiO_2 thin films.

1. Introduction

There is an increasing interest in extending functional film properties. With properties such as high refractive index, wide band gap and chemical stability, TiO_2 can be used in a large range of applications [1–3]. Furthermore, TiO_2 can be deposited on a variety

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Table 1
Thin film Processing conditions for the deposition of titania samples by ion beam sputtering.

Sample	Substrate	Ar Partial Pressure(Pa)	O_2 Partial Pressure(Pa)	T (K) of the substrate holder	Deposition time (Hrs)	Film Thickness(μm)
1	Si	2.0×10^{-2}	0.5×10^{-2}	722	3	1.3
2	Si	2.13×10^{-2}	0.37×10^{-2}	722	3	1.3
3	Si	3.0×10^{-2}	0.5×10^{-2}	722	3	1.3
4	Si	4.0×10^{-2}	0.5×10^{-2}	350	3	2.2
5	Si	4.0×10^{-2}	0.5×10^{-2}	722	3	1.3
[a]6	Si	1.5×10^{-2}	1.0×10^{-2}	350	3	1.3
7	Si	1.2×10^{-2}	1.3×10^{-2}	298	3	0.3

[a] Sample 6 – O_2 ion assist conditions: extra energy added by the use of a second ion gun.

of substrates, such as glass slides, silica glass, silver, porcelain bricks, metal panels, etc. The resulting coatings possess great potential for various industrial applications, including photocatalytic surfaces [4,5].

As one of the most important wide-band-gap (Energy >3 eV) oxides, titania has been extensively academically studied and technologically researched for decades. The electrochemical properties of titanium dioxide are applied to photovoltaic solar cells and gas sensors. Because of its high dielectric constant, hardness, and transparency, TiO_2 thin films are usable for storage capacitors in integrated electronics, protective coatings, and optical components [6,7].

Numerous key applications of titania are strongly related to the structure and optical properties of TiO_2. TiO_2 is known to have different crystalline forms; anatase, rutile and brookite. Films having dense structure are usually used for solar cell applications while porous films are used for gas sensors. The rutile phase is known to be the most thermodynamically stable phase and has a high refractive index which makes it the most appropriate for protective coatings [8]. The anatase phase is more reactive with ultraviolet light; therefore, it is used for photocatalysis [9–12]. Amorphous, TiO_2 films are used in biomedical fields by reason of its blood compatibility [13].

TiO_2 thin films and indeed powders have been and are fabricated by different methods for numerous applications [14–29]. It is well known that TiO_2 can exist in a number of crystalline forms with differing physical properties and that the choice of the deposition process has a significant impact on the structure of the film. Generally, TiO_2 films change from amorphous to anatase and then rutile depending on the temperature of calcination. Indeed reports suggest that the structural and optical properties are strongly related to the temperature of calcination [14]. Ion-assisted deposition of materials can produce coatings with improved properties since the ion-assistance can provide incident atoms with additional energy. This added energy can modify the nucleation process, improve film adhesion, increase film density, stimulate mixing of alloy materials to form metastable compounds, trigger phase changes, influence film stress and change film microstructure [15–30]. All these factors can be utilized to modify the optical and physical properties of a coating [15].

In the fabrication of visible light responsive thin films, for example, by sintering and impregnation with solutions of modifiers SEM images showed the formation of compact layers of titanium dioxide with particles of diameter within 15–30 nm. The

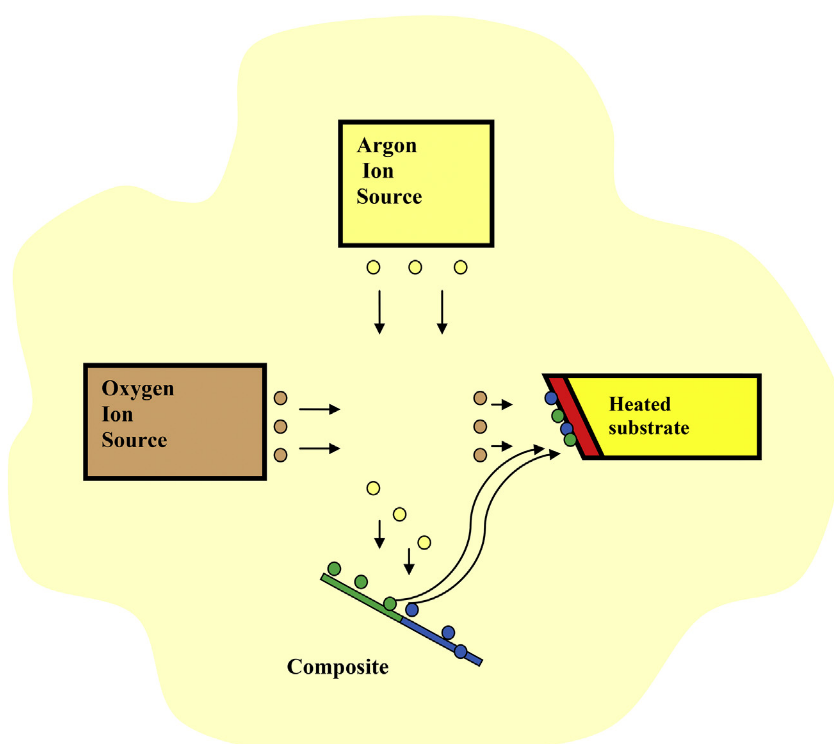

Fig. 1. Ion beam IAD system [22].