Photocatalysis in Carbon doped TiO_2 thin films grown by DC magnetron sputtering

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Abstract
Pure and carbon doped TiO_2 thin films were grown by reactive pulsed dc magnetron sputtering of titaniumin argon, oxygen and carbondioxide atmosphere. Sputtering density, argon and oxygen flow rates were maintained at 5W/cm^2, 10 sccm and 6sccm, respectively whereas the carbondioxide flow rate was varied. The thin films were investigated for their structural, optical, morphological and photocatalytic properties. Carbon doped TiO_2 thin films show a near visible bandedge (390 nm) and higher photocatalytic efficiency; degradation rate of methylene blue is 0.799 µmol/l.d.

Keywords: *Photocatalysis, Sputtering, Thin films, and Oxides*

Introduction

Titanium dioxide thin films have been used in wide range of applications like dye sensitized solar cells, gas sensors, electrochromic windows, waste water treatment, etc. Recently, photocatalysis based applications of TiO_2 have gained importance in environmental protection as they could effectively decompose organic and inorganic pollutants. Pure TiO_2 is active onlyunder ultraviolet light, whose energy is greater

than the band gap of TiO_2(3.2 eV). The effective utilization of visible light occupying the main part of solar spectrum is one of the important subjects for increased utility of TiO_2. Recently, some groups have demonstrated band gap shift in TiO_2 by substitution of non-metal atom such as nitrogen, fluorine and sulphur for oxygen [1-3]. In order to improve the photoreactivity of TiO_2 and to extend its absorption edge into the visible-light region, doping of various transition metal cations has been intensively attempted [4-6]. However, carbon doping in titanium dioxide has proved to be been an efficient method for band shift in visible region and is reported by several researchers [7-10]. In the present investigation, we have deposited pure and carbondoped TiO_2 thin films by reactive pulsed DC magnetron sputtering, a versatile and industrially viable deposition technique. The effect of carbon doping on the structural, optical, morphological and photocatalytic properties of TiO_2 thin films has been addressed in detail.

2. Experimental details

2.1. Preparation

Pure and carbon doped titanium dioxide thin films were deposited on silicon and soda lime glass substrates by reactive pulsed DC magnetron sputtering using a modified commercial vacuum system (PLS 570, Pfeiffer). Pure TiO_2 samples have been deposited by sputtering metallic titanium (99.8 %) in the presence of argon and oxygen atmosphere. The flow rates for argon and oxygen were kept constant at 10 sccm and 6 sccm, respectively. The target was powered by a pulsed DC magnetron power supply operating at a constant power density of 5 W/cm². The pulsing frequency and duty cycle were maintained at 50 x 10^3Hz and 0.75 respectively. Carbon dopingwas obtained by flowing carbon dioxide into the chamber at controlled flow rates of 2 sccm and 3 sccm, respectively. In the present study, 3 sets of samples are investigated. They are (i) pure TiO_2 films; coded as TO (ii) carbon doped TiO_2 thin films deposited with CO_2 flow rate of 2 sccm; coded as CTO1 and (iii) carbon doped TiO_2 thin films deposited with CO_2 flow rate of 3 sccm; coded as CTO_2. The distance between target and the substrate is kept at 60 mm.

2.2. Characterization

The crystal structure of pure (TO) and carbon doped TiO_2 (CTO1, CTO2) thin films was investigated by X-ray diffraction (Seifert FPM, URD-6) using Cu Kα radiation. The surface morphology was studied by field emission scanning electron microscopy (Zeiss, Gemini 982). The optical measurements were done using UV-Vis spectrophotometer (Lambda 950, Perkin Elmer). The photocatalytic activity was tested by methylene blue (MB)bleaching reaction. Pure and doped TiO_2 samples of size 20 x 20 mm^2 immersed in 20 ml of methylene blue were irradiated with ultraviolet light (P_{UV-A}=1 mW/cm^2) and the MB concentration was determined by photometric transmission measurement in the visible range of spectrum (Haze Gard plus, BYK-Gardner).

3. Results and Discussion

3.1. Structural and optical properties

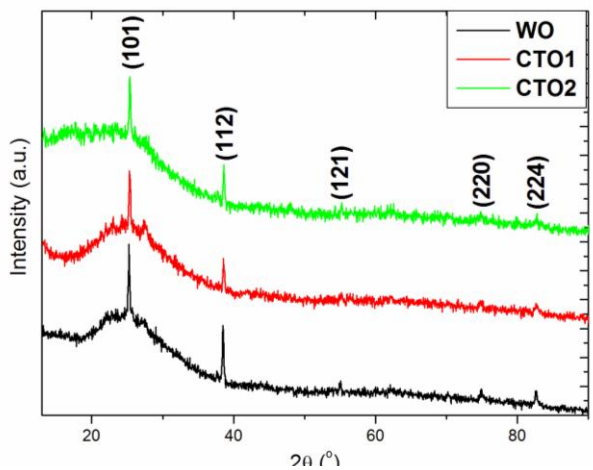

Figure 1: XRD pattern of pure (TO) and carbon doped titanium dioxide (CTO) thin films

The XRD spectrum of pure and carbon doped TiO_2 thin films are shown in Figure 1. All the as-deposited samples are X-ray amorphous in nature whereas the films annealed at 450 °C for 4 hours are found to be highly crystalline with prominent peaks from (101), (112), (121), (220) and (224)planes corresponding to anatase TiO_2 (ICSD 9852). With carbon doping, the intensity of peaks is found to decrease implying a fall in crystallinity. There are no peaks corresponding to carbon clusters or mixed phases. This could be attributed to the low content of carbon.Figure 2 shows the transmittance and absorbance spectra of pure and carbon doped TiO_2 thin films in the wavelength range of 300 to 850 nm. As evident from the figure, the samples are found to be highly transparent (~ 85%) in the entire visible range. In the present investigation, the absorbance estimated from the transmittance and reflectance measurements is accurate since for reflectance it's not the sample position but the optics is adjusted.

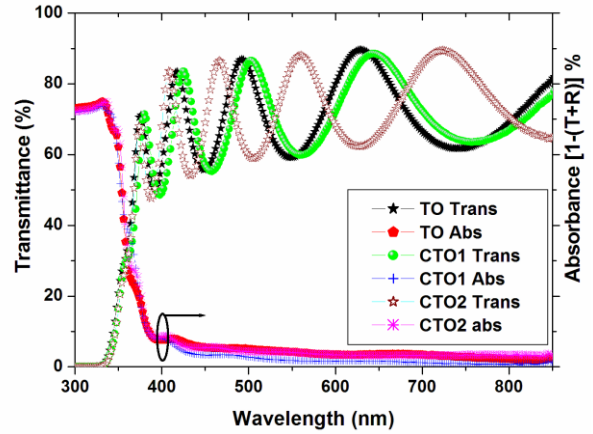

Figure 2: Transmittance and absorbance spectra of pure (TO) and carbon doped titanium dioxide (CTO) thin films

The absorption edge of pure TiO_2 (TO) is around 372 nm whereas the carbon doped TiO_2samples CTO1, CTO2, have absorption edges in the near visible range with values around 388 nm and 392 nm, respectively. The thicknesses of the samples TO, CTO1 and CTO2 are found to be 520 nm, 508 nm, and 502 nm,respectively.

3.2. Morphology

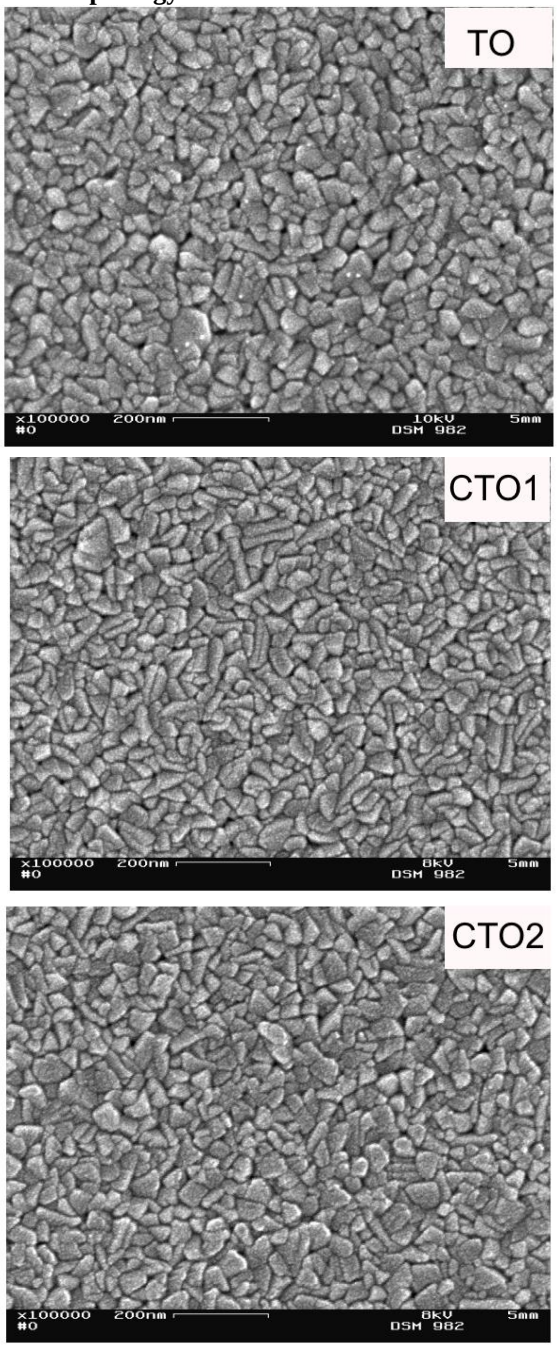

Figure 3: Transmittance and absorbance spectra of Pure (TO) and carbon doped titanium dioxide (CTO) thin films

The Scanning electron microscopy images of pure and carbon doped TiO_2 thin films are shown in Figure 2 (a -d). The surface morphologyof pure TiO_2 shows the presence of irregular shaped particulates with an average particle size of 38 nm. However, the carbon doped TiO_2 thin films show

elongated surface structures with an average particle size of 53 nm and 45 nm for CTO1 and CTO2, respectively.

3.3. Photocatalytic properties

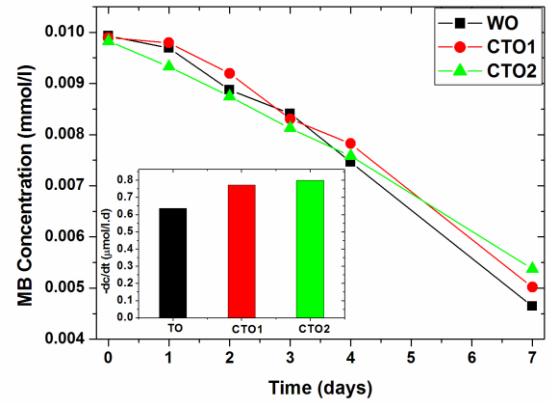

Figure 4: Photocatalytic degradation of methylene blue (MB) bypure (TO) and carbon doped titanium dioxide (CTO) thin films

The photocatalytic performance of pure and carbon doped TiO_2 thin films was studied by the decomposition of methylene blue exposed to ultraviolet radiations. As shown in Figure 4, all the samples show photocatalytic activity. However, carbon doped TiO_2 thin films (CTO2) are found to be better photocatalytic than the other samples (TO, CTO1); the decomposition rate of Methylene blue (MB) by TO, CTO1 and CTO2 are -0.636, -.772 and -.799 μmol/(l.d), respectively.

4. Conclusion

Carbon doped TiO_2 thin films with elongated surface structures were grown by reactive pulsed DC magnetron sputtering. The films are highly crystalline and are found to settle in anatase phase. Of all the samples, carbon doped thin films (CTO2) have a near visible band edge of 392 and methylene blue degradation rate of -.799 μmol/(l.d).

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