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Effect of Fe doping on TiO_2 films prepared by spin coating

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Abstract

Iron-doped titanium dioxide thin films were coated on fluorine-doped tin oxide coated glass using the spin coating technique. The concentration of the dopant was varied up to 7 mol% iron (metal base). The films were characterised for their structural, morphological, and optical properties. Glancing angle X-ray diffraction and laser Raman microspectroscopy indicate that the films consisted solely of the anatase polymorph of titanium dioxide, without any contamination phases, such as iron oxide. Field emission scanning electron microscopy indicates that the films were microstructurally homogeneous and fully dense, with grains in the size range of ~10–20 nm. UV-VIS spectrophotometry shows that the optical indirect band gap of the films decreased with increasing iron doping (3.36 eV for undoped and 2.95 eV for 7 mol% Fe).

Keywords: Titanium dioxide; Fe doping; Spin coating; X-ray photoelectron spectroscopy

1. Introduction

Over the last few decades, titanium dioxide (TiO_2, titania) has been investigated extensively for a range of applications owing to a number of advantages, which include long-term environmental stability, nil toxicity, inertness to acids, and significant photocatalytic behaviour [1]. Furthermore, TiO_2 has been found to be the most suitable material for a wide range of environmentally beneficial applications, including water and air purification [2,3]. However, TiO_2 is a wide band gap ($E_g = 3.2$ eV) semiconductor [4], and so it can absorb only in the ultraviolet (UV) region of sunlight; this indicates that only ~5% of incident sunlight can be absorbed [4]. Therefore, in order to improve the photocatalytic activity of TiO_2 in the visible region, modification of the band gap by doping with transition metals, including Cr [5], Mn [4], Fe [6], and Zn [7], has been studied. Of the preceding dopants, Fe has attracted strong interest owing to its octahedral trivalent radius of 0.079 nm, which is similar to that of octahedral tetravalent Ti (0.075 nm) [8]. Therefore, it can be inferred that Fe^{3+} ions can be incorporated in the Ti^{4+} sublattice of TiO_2, which also could enhance oxygen vacancy formation, potentially leading to an improvement in the photocatalytic performance [9].

Fe-doped TiO_2 thin films can be prepared by several techniques, including sputtering [10], metal organic chemical vapour deposition (MOCVD) [11], dip coating [12], ultrasonic spray pyrolysis [13], and spin coating [14]. The latter is considered as one of the most advantageous techniques due to its effectiveness, versatility, and practicality. Importantly, it does not require a vacuum system since the process can be carried out at atmospheric conditions.

In the present work, Fe-doped TiO_2 films were deposited on F-doped SnO_2-coated glass (FTO-coated) using spin coating. The effect of the dopant concentration was investigated in terms of the structural, morphological, and optical properties of the resultant thin films.

2. Methodology

Solution precursors were prepared using Ti isopropoxide (TIP, Reagent Grade, 97 wt.%, Sigma–Aldrich) dissolved in isopropanol (Reagent Plus, ≥99 wt.%, Sigma–Aldrich) at a Ti concentration of 0.1 M (2.8 g of TIP diluted to 100 mL volume with isopropanol); the solutions were mixed by stirring in a Pyrex beaker at 400 rpm with a Teflon-coated rod for 10 min without heating. The Fe dopant concentration was varied to 1, 3, 5, and 7 wt.% Fe (metal basis relative to Ti isopropoxide) by

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adding $FeCl_3$ (Reagent Plus, ≥99 wt.%, Sigma–Aldrich) to the solution with hand stirring. The Fe was added on the basis of stoichiometric TiO_2; that is, there was no compensatory decrease in the Ti levels. Spin coating (Laurell *WS-65052*) was done by rapidly depositing ∼0.2 mL (ten sequential drops) of solution onto an FTO-coated glass substrate (WuHan Geao Instruments Science & Technology Co., Ltd., China) spun at 2000 rpm in air. The film was dried by spinning for an additional 15 s. This process was repeated four more times (*viz.*, ∼1 mL; fifty drops) in order to obtain as-deposited thin films of ∼500 nm thickness. Subsequent annealing was done in a muffle furnace at 500 °C with a heating rate of 5 °C/min and soak time of 5 h, followed by natural cooling.

The mineralogies of the films were determined by glancing angle X-ray diffraction (GAXRD, Phillips *X'pert Materials Research Diffraction*, CuKα, 45 kV, 40 mA, step size 0.02° 2θ speed 6°/min 2θ) and laser Raman microspectroscopy (He–Cd UV laser excitation source of wavelength 442 nm, Renishaw *inVia*). Field emission scanning electron microscopy (FESEM, Nova *NanoSEM 230*; Cr-coated, secondary electron emission mode, 2 kV accelerating voltage) was used to investigate the morphologies of the films. The chemical compositions and metal valences were investigated using X-ray photoelectron spectroscopy (XPS, Thermo Scientific, *ESCALAB250Xi*). The transmission in the ultraviolet-visible (UV-VIS) range was determined using a dual-beam spectrophotometer (Perkin Elmer *Lambda 35*); the optical indirect band gap was calculated from these data using the method of Tauc and Menth [15].

3. Results and discussion

The GAXRD patterns, given in Fig. 1, show that, with increasing Fe dopant levels, the anatase peaks become broader and smaller, which suggests decreasing degree of crystallinity. Further, the laser Raman microspectra (data not shown) tend to confirm the GAXRD results in that they also show a decrease in anatase peak intensities with increasing Fe dopant levels. Since the Fe was added to stoichiometric TiO_2, it is clear that the accommodation of the former in the lattice, whether substitutional or interstitial, results in structural distortion and concomitant decrease in crystallinity [9].

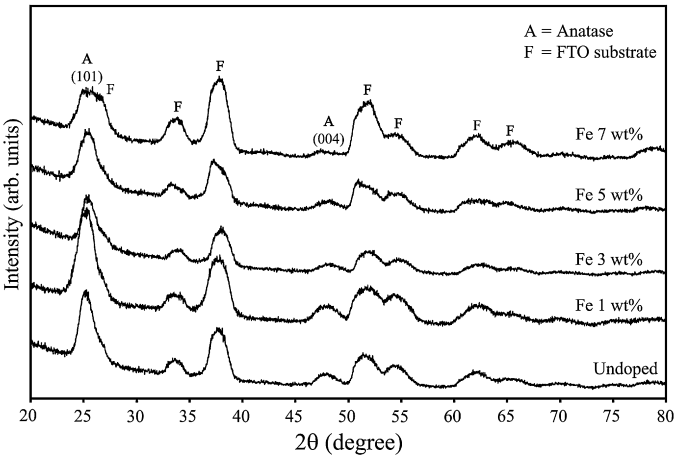

Fig. 1. Glancing angle X-ray diffraction data of Fe-Doped TiO_2 Films.

Fig. 2 shows FESEM images of the films containing the different Fe dopant levels. These data show that the films are microstructurally homogenous, with no pinholes, and the grains were in the size range of ∼10–20 nm. It is clear that Fe^{3+} had no effect on enhancing the grain growth that accompanies the anatase → rutile phase transformation, which generally is considered to occur at temperatures ≥600 °C, although it can occur <500 °C [9].

Table 1 shows the results of the XPS measurements, which reveal that contamination of the film by the substrate occurred. It should be noted that Fe^{3+}, Sn^{4+}, and Na^{1+} are known to enhance the anatase → rutile phase transformation [9] while Si^{4+} is known to suppress it.

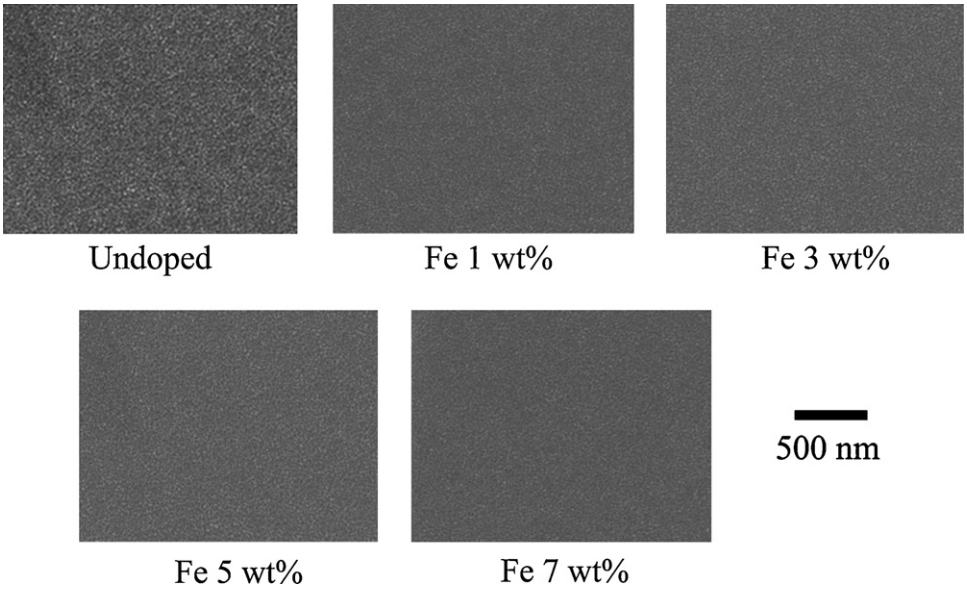

Fig. 2. Field emission scanning electron microscopy images of Fe-Doped TiO_2 Films.

Table 1
Summary of analytical data.

Fe dopant level added (wt.%)	Dopant/contaminant level determined by XPS (wt.%)				Transparency (%)	Optical indirect band gap (eV)
	Fe^{3+}	Sn^{4+}	Si^{4+}	Na^{1+}		
0	0.00	1.15	1.37	1.56	70–80	3.36
1	0.54	1.15	0.00	1.29		3.24
3	1.82	1.88	0.00	1.51		3.13
5	3.01	1.41	0.00	1.83	50–60	3.04
7	5.57	1.70	0.00	1.46		2.95

Since Si^{4+} was detected only in the undoped film, while Fe^{3+}, Sn^{4+}, and Na^{1+} were detected in all doped films, the retention of anatase might be expected. It is likely that the annealing conditions of 5 h at 500 °C were insufficient to cause the phase transformation.

The XPS data also reveal other features:

- The Fe^{3+} levels were lower than added initially. This probably is a result of the diffusion of this ion into the substrate. Diffusion of Fe^{2+} and Fe^{3+} into fused silica glass at only 400 °C has been reported before [16].
- The films were contaminated by Sn^{4+} owing to diffusion from the FTO coating on the substrate. The absence of a trend indicates that this is a relatively consistent effect, unaffected by the Fe dopant level.
- The films also were contaminated by relatively consistent levels of Na^{1+} owing to diffusion from the soda-lime–silica substrate. The diffusion of the small and mobile Na^{1+} ion is well known.
- Contamination of the undoped film only by Si^{4+} is notable. Since Fe^{3+} is absent in the undoped film and Sn^{4+} is present, this observation suggests Sn^{4+} is not causative and that counter-diffusion and/or blocking of Ti^{4+} lattice sites by Fe^{3+} may be responsible for suppression of Si^{4+} diffusion and resultant contamination of the doped films.

The UV–VIS spectra of the films are shown in Fig. 3. It can be seen that, in both the UV (≤400 nm) and visible (400–800 nm) regions, the transmission generally decreased with increasing Fe dopant levels. Further, the absorption edge shifted to longer wavelengths with increasing Fe dopant levels, thereby increasing the radiation absorption. The presence of interference fringes in the transmission spectra indicates that the films

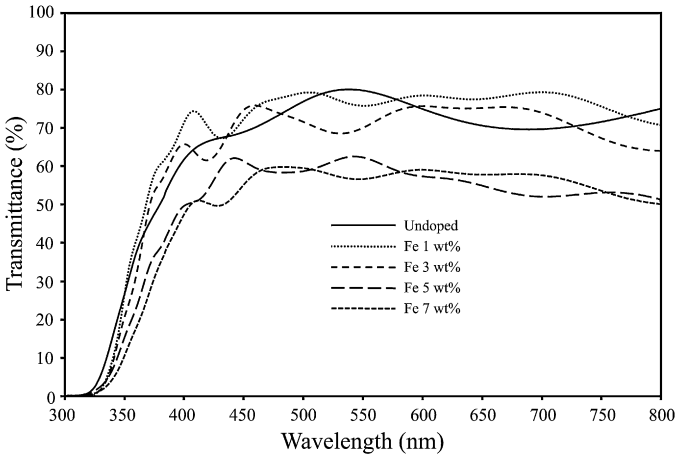

Fig. 3. UV–VIS spectra data of Fe-Doped TiO_2 Films.

are smooth and microstructurally homogenous [17]. These data confirm the observations of the FESEM analyses.

The optical indirect band gap of films can be calculated from UV-VIS spectrophotometry data, the details of which are described elsewhere [13,15,18]. The values obtained from these data are listed in Table 1.

Fe^{3+} is known to create shallow trapping sites at the donor and acceptor levels [19], as shown in Fig. 4 (left). This effective decrease in the band gap means Fe-doped films can absorb more light in the visible region than undoped films, thereby increasing the efficiency of the photocatalytic performance of the material.

The calculated thermodynamic stability diagram of Fe–O, as given in Fig. 4 (right), shows that the annealing conditions of 500 °C in air result in the existence of Fe^{3+} only. The XPS data

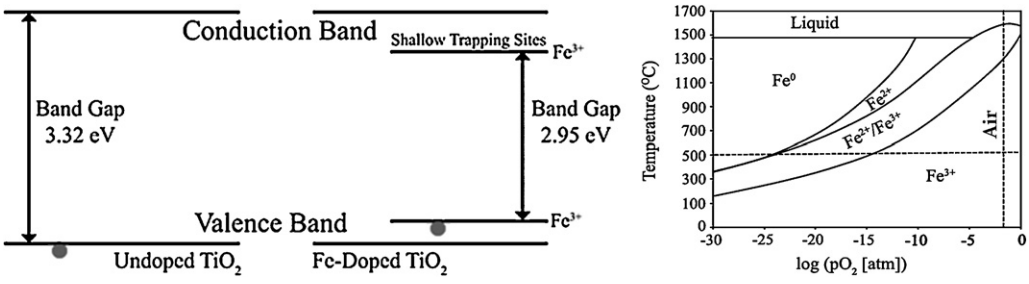

Fig. 4. Hypothetical band structure of Fe-doped TiO_2 (left) and thermodynamic stability diagram for Fe–O (right).

confirm this, showing only Fe^{3+} and the absence of other ions, such as Fe^{2+} and Fe^{4+}, which is common with previous studies [20,21].

4. Summary and conclusions

Fe-doped TiO_2 thin films coated on FTO substrates using spin coating have been produced. The thin films were reproducible and high quality, as shown by the consistent bulk densities, thicknesses, grain sizes, surface profiles, UV–VIS spectra, and dopant retention of all of the thin films. The GAXRD and laser Raman microspectroscopy analyses show that the films consisted of anatase only, with no formation of secondary phases, such as Fe_2O_3. Further, these results indicate that the presence of incorporated Fe results in lattice distortion. The FESEM images show that the grain size of the films was consistent and in the range ∼10–20 nm. The UV–VIS data show that the films were relatively transparent and had smooth surfaces. Increasing Fe dopant levels caused a significant decrease in the optical indirect band gap. The contamination of the films by Sn^{4+}, Na^{1+}, and/or Si^{4+} is an important variable that requires further investigation. The effect of Si^{4+} is particularly important because thin films deposited on quartz and glass following by annealing for recrystallisation, which is the vast majority, are subject to what is likely to be a near-universal contaminant.

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