RP Materials: Proceedings
Vol. 1, Part 1 (2022) pp. 1–4
e-ISSN:

RESEARCH PLATEAU PUBLISHERS

Cite this article: M. Singh, Optical characterization of iron and titanium oxide doped titanium oxide thin films prepared by spray pyrolysis method, *RP Materials: Proceedings* Vol. 1, Part 1 (2022) pp. 1–4.

Original Research Article

Optical characterization of iron and titanium oxide doped titanium oxide thin films prepared by spray pyrolysis method

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****Selection and Peer-Review under responsibility of the Scientific Committee of the National Conference on Advanced Engineering Materials (NCAEM 2022).**

ARTICLE HISTORY
Received: 5 Aug. 2022
Revised: 9 Nov. 2022
Accepted: 10 Nov. 2022
Published online: 27 Dec. 2022

KEYWORDS
TiO_2 and Fe doped TiO_2 thin films; laser Raman spectroscopy; Rutherford backscattering measurements.

ABSTRACT
The present paper examines the characterization of Fe and TiO_2 doped TiO_2 thin films produced by spray pyrolysis in terms of their optical and physical characteristics. Undoped TiO_2 thin film was created by alternately misting distilled water and a weak acidified titanium isopropoxide solution (pH < 2) onto a heated (280°C) glass substrate. Fe-doped TiO_2 thin film was created by combining the necessary amount of aqueous $Fe(NO_3)_3$ solution with titanium isopropoxide solution (pH < 2), then spraying the mixture on a heated (280°C) glass substrate while alternating with distilled water. Fe-doped and undoped TiO_2 films were deposited, and both were then annealed at 400°C in air for 15 minutes. Using a Philips X' pert x-ray diffractometer with a Cu target, fixed divergence slit, and gas sealed proportional counter as an x-ray detector, these were evaluated for their ability to identify phases. Via Reinishaw Laser Raman spectrometer, Raman spectra were captured. The transmittance/absorbance spectrum of films was documented with the help of varian UV-Visible spectro-photo-meter. Rutherford backscattering measurements of these films was performed using a 3.043 MeV He^{++} ion.

1. Introduction

Titanium oxide is a substance with low costs, excellent chemical stability, and little toxicity. TiO_2, a semiconducting material having band gap energy equal to 3.20 eV, emits holes and electrons in the valence and conduction bands when exposed to UV light with a wavelength larger than 3.20 eV (380 nm). Inducing catalytic processes on the catalyst surfaces are the electrons' high reduction potential and the holes' extremely large oxidation potential. Unfortunately, only 3-5% of high intensity UV light (of wavelength 380 nm or less) is present in the sun spectrum that reaches the earth's surface, which restricts the use of TiO_2 photo-catalyst within buildings. Hence, by doping transition metal ions into it, tremendous attempts are undertaken to lower its band gap energy so that it can absorb visible radiation [2]. Reduce the rate of hole and electron re-combination by the presence of ions functioning as electron or hole traps in order to produce the improved photo-physical activity. According to reports [3] iron-doped TiO_2 exhibits both a stunning photo-killing effect on cancer cells as well as significant photo-catalytic activity. TiO_2 can be used as an oxygen sensor in a variety of applications in the automotive, metallurgical, environmental, and biological sciences, among others, thanks to Fe doping in TiO_2, which also affects the material's optical and photo-catalytic properties [4]. Designing an appropriate process for producing thin films of iron doped TiO_2 is important so as to attain better photo-physical characteristics and photochemical activity. This work examines the study of TiO_2 and Fe-doped TiO_2 thin films produced via spray pyrolysis method in terms of their physical and optical properties.

2. Experimental

Starting ingredients included $Fe(NO3)_3$ and titanium iso-propoxide (TIP, Aldrich). Undoped TiO_2 thin film was created by alternately misting distilled water and a weak acidified titanium iso-propoxide solution (pH < 2) onto a heated (280°C) glass substrate. Fe-doped TiO_2 thin film was created by combining the necessary amount of aqueous $Fe(NO_3)_3$ solution with titanium iso-propoxide solution (pH < 2), then spraying the mixture on a heated (280°C) glass substrate while alternating with distilled water. Fe-doped and undoped TiO_2 films were deposited, and both were then annealed at 400°C in air for 15 minutes. Using a Philips X' pert x-ray diffractometer with a Cu target, fixed divergence slit, and gas sealed proportional counter as an x-ray detector, these were evaluated for their ability to identify phases. Via Reinishaw Laser Raman spectrometer, Raman spectra were captured. The transmittance/absorbance spectrum of prepared films was documented with the help of varian UV-Visible spectro-photo-meter. Rutherford backscattering measurements of these films was performed using a 3.043 MeV He^{++} ion.

3. Results

The x-ray diffractograms of thin films of TiO_2 via Fe and TiO_2 doping, that were annealed at 400°C are depicted in

Figure 1. The anatase phase of TiO_2 produces the diffraction lines seen at d = 3.51 Å, d = 2.37 Å, and d = 1.89 Å. When 5 at. wt% of Fe was doped into the lattice, the intensity of these lines dropped, indicating an increase in short range order in the system. Table 1 contains the laser Raman spectra that were obtained for the thin films mentioned above. The spectra were taken between 50 and 1000 cm^{-1}. Despite the presence of numerous bands, only two strong bands: 145 and 656 cm^{-1}, were de-convoluted and are listed in Table 2. According to the table, Raman bands at 635, 512, 395, and 200 cm^{-1} are not seen in Fe-doped TiO_2 films as they are being deposited, but they do reappear after being annealed at 400°C. Figure 2a displays the UV-visible absorption spectra that were obtained for these films. Thin films of TiO_2 and Fe in TiO_2 exhibit absorbance at 300 nm wavelengths both as-deposited and after being annealed. Fe doping and annealing of thin TiO_2 films, however, broaden the absorption band. The Rutherford backscattering method was used to analyse the composition of these films, and the spectra for the films are displayed in Fig. 2b. The oxygen to titanium ratios for Fe and TiO_2 doped TiO_2 thin films, and TiO_2 powder were determined to be 2.0, 0.5, and 0.67, respectively.

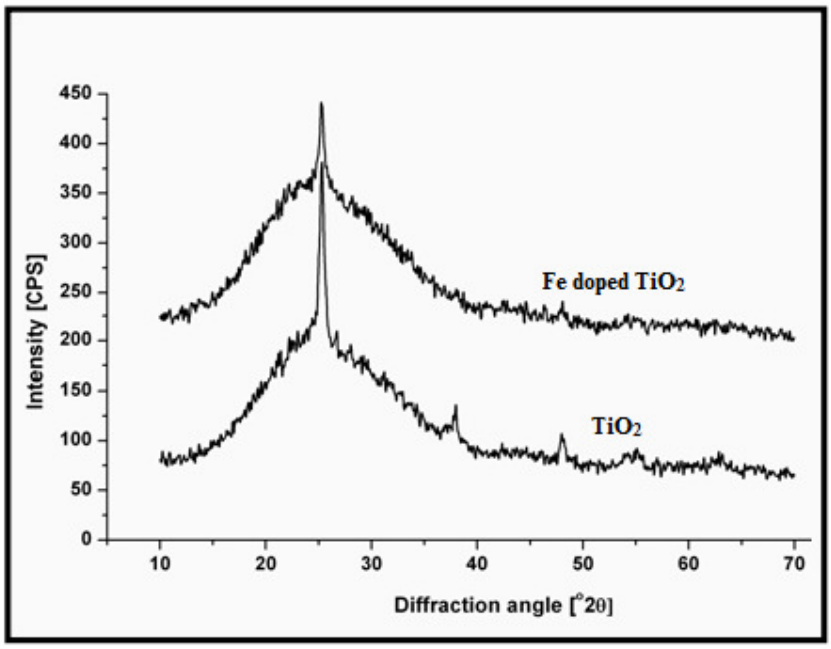

Figure 1: XRD pattern of Fe doped TiO_2 and TiO_2 films.

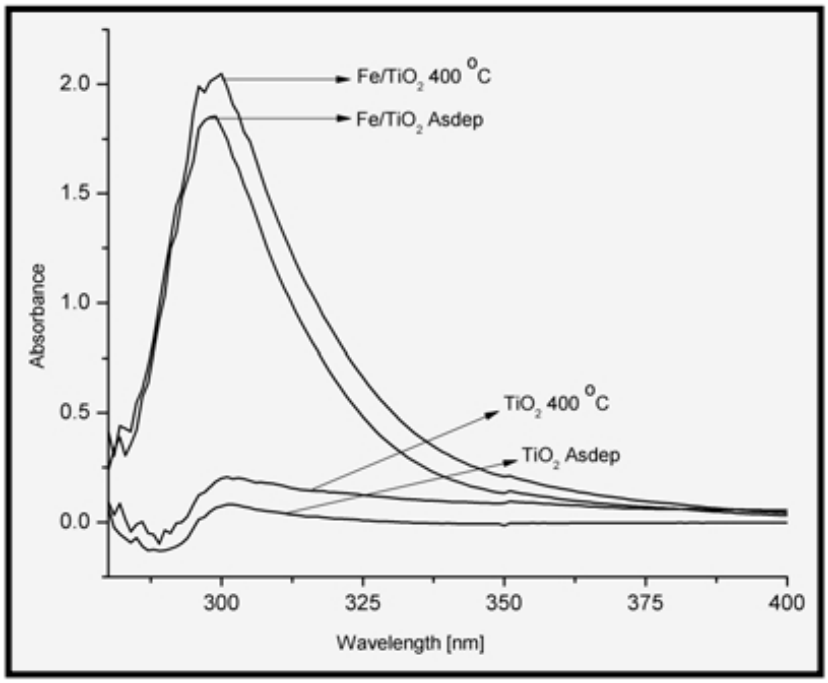

Figure 2a: Absorbance spectra of as-deposited and annealed of Fe and TiO_2 doped TiO_2 films.

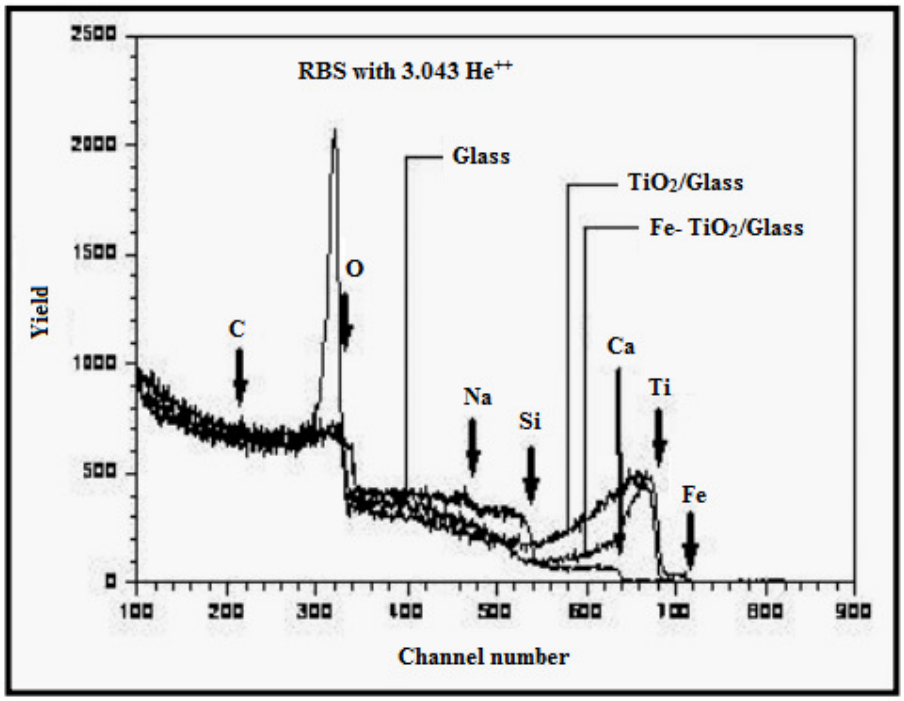

Figure 2b: Rutherford back scattering spectra of Glass, Fe and TiO_2 doped TiO_2 films.

Table 1: Raman shifts (in cm^{-1}) in TiO^2 thin films.

	Assignments				
	E_g	B_{1g}	B_{1g}	E_g	E_g
TiO_2 –as- deposited	635	511	395	200	145
TiO_2 annealed	635	516	400	188	145
Fe doped TiO_2-as-deposited	No obs.	No obs.	No obs.	No obs.	145
Fe doped TiO_2 annealed	635	516	392	200	145

Table 2: Observed Raman bands at 145 and 635 cm^{-1}.

		Wave number 145 cm^{-1} E_g (ν_1)			Wave number 636 cm^{-1} E_g (ν_6)		
TiO_2 asdeposited	Peak position	145	152	No obs.	636	650	No. obs.
	FWHM	8.36	16.15	No. obs.	21.17	42.36	No. obs.
TiO_2 400°C	Peak position	145	157	170	617	640	660
	FWHM	9.84	10.02	10.66	34.54	20.86	25.40
Fe doped TiO_2 asdeposited	Peak position	145	156	166	No. obs.	No. obs.	No. obs.
	FWHM	11.17	7.7	14.05	No. obs.	No. obs.	No. obs.
Fe doped TiO_2 400°C	Peak position	145	155	175	603	636	654
	FWHM	9.62	14.98	27.17	22.65	27.60	41.28

4. Discussion

When the films are doped with iron, the x-ray diffraction patterns reveal that they are nano-crystalline in nature, with crystallite sizes over 19 to 15 nm. Owing to crystallites' decreased size as well as increased surface area, the Fe doped TiO_2 (Anatase) phase's increase in short range order can be attributed to this. When the films were annealed at 400°C in air, the oxygen to titanium ratio decreased in the Fe doped sample, indicating increased disorder in the film. RBS testing results have also verified the existence of Fe. The RBS study was used to calculate the dimensions of the films, which were determined as 166 nm for TiO_2 and 116 nm for Fe doped TiO_2.

Several researchers have examined the laser Raman spectra on nanocrystalline TiO_2 [5-8]. The majority of the study is focused in the high frequency area, though. We can only observe in the low frequency range of 50 to 1000 cm^{-1}. There have been identified several bands. Yet, it's noteworthy to notice that when as-deposited films were examined, iron incorporation into TiO_2 altered the spectral characteristic. There may be iron in the lattice, which increases the short-range order in the system, explaining why these low frequency bands are absent. However, after annealing, the Raman bands at 635, 515, 393, and 198 cm^{-1} re-emerge due to a drop in the short range order. X-ray diffraction experiments, which show the improvement in short range order after annealing, provide support for this conclusion. Interesting characteristics can be seen in the de-convoluted Raman spectra. The band at 145 cm^{-1} may represent the lattice vibration of the anatase phase, which

is unaffected by the doping of iron or annealing of the film. De-convolution, however, produces three bands at 145, 157, and roughly 171 cm^{-1}. The 171 cm^{-1} band's complete width at half its maximum increased from 10.65 to 27.18 cm^{-1}. In Fe doped TiO_2, the 145 and 635 cm^{-1} bands' intensities decreased, and the FWHM widened. As iron is doped into TiO_2, RBS spectra demonstrate a drop in the O/Ti ratio. In the TiO_2 (Anatase) structure, oxygen atoms are octahedrally coordinated with six other oxygen atoms and have three nearest neighbours. The disorderness increases when iron is doped into the lattice because iron partially replaces the Ti atoms. This results in the absence of noticeable bands in the 200 to 800 cm^{-1} area of the Raman spectrum. The Raman bands resurface in annealed Fe doped TiO_2 films as a result of the reduction in disorderness caused by annealing, which is visible in the XRD patterns. As titanium atoms coordinate in a four-fold coordination with oxygen atoms, lowering Ti-Ti distances and adding some randomness in the film, the absorption spectrum of Fe doped TiO_2 exhibit an increase in absorbance [5].

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