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Nanostructured Anatase Titania Thin Films Prepared by Sol-Gel Dip Coating Technique

Research Article

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Abstract. Anatase titania thin films were deposited on glass substrates. The substrates were dipped matched dipped into the solution under vigorous stirring. The films were dried at room temperature. *Oley amine* (OM) was used as a surfactant in the synthesis part and it was vigorously stirred with *titanium isopropoxide* (TIP) at room temperature. The film samples were annealed at 550 °C for 15 hours. *X-ray diffraction* (XRD) and Raman spectroscopy were used to study the structural properties of samples. The optical properties of samples were investigated by means of *ultraviolet visible* (UV vis) spectroscopy. XRD results illustrated the amorphous structure and pure anatase phase of TiO_2 for as deposited and annealed thin films samples and these results were further confirmed by Raman spectroscopy. UV-visible corroborates the energy band 3.26 and 3.22 eV for as prepared and sintered TiO_2 thin films which simply refers to the change in crystal structure of anatase titania. Furthermore, both samples had high transmittance; almost 78-86%.

Keywords. Nanostructured Titania thin films; Dip-coating technique; Raman spectroscopy

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1. Introduction

Titanium dioxide (TiO_2) is an excellent n-type oxide that has been vastly investigated due to its outstanding electrical and optical properties such as large band gap, and high dielectric constant [1–6]. It is low cost and non-toxic material [7, 8] which can be easily doped with active ions [1, 6]. The titania films have excellent properties such as good durability, high thermal and chemical stability [9–12]; therefore, they are suitable for producing antireflection and optical coatings [1]. TiO_2 has been used instead of toxic lead oxides as pigments for white paint, printing ink, plastics, paper, food and cosmetics [8]. It is used as a biomaterial because it has a good compatibility with the human body [7]. Titania is a versatile material and has been extensively studied in photocatalysis [2], photonic crystals, sensors [3, 11], light scattering [1] and liquid crystal displays [10]. When TiO_2 is exposed to the light, the activated oxygen is formed which is useful to oxidize and decompose organic compounds, nitrogen oxides, and to kill the bacteria [6–8]. Some of the properties of TiO_2 films such as the optical and electrical properties are sensitive to the methods of films preparation. Variety of methods such as sputtering, chemical vapour deposition, electron beam evaporation, spray paralysis, hydrothermal, sol-gel and dip-coating have been used for the preparation of titania films [5, 11]. The sol-gel dip coating route was used due to its low cost, easy processing, control over stoichiometry and crystallite size, particle morphology, crystalline phase, surface chemistry by regulating the solution composition, reaction temperature, and ageing time. It is a low power consumption technique which also gives better purity, homogeneity, felicity, [2], and has ability for coating the large and complex areas [1, 7, 9]. This study aimed to evaluate the synthesis of nanostructured TiO_2 thin films deposited onto glass substrate by dip-coating technique at room temperature and discuss their structural and optical properties.

2. Experimental Details

2.1 Materials

Titanium isopropoxide (TIP, $C_{12}H_{28}O_4Ti$), Oley amine ($C_{18}H_{37}N$), Acetone, C_3H_6O, Methanol, CH_4O were used for the preparation of TiO_2 thin films. These materials were purchased from Sigma Aldrich and used as received.

2.2 Preparation of Nanostructured TiO_2 Thin Films

Titanium isopropoxide (TIP) was incrementally added to a mixture of 20 ml methanol and *Oley amine* (OM). The molar ratio of Methanol/TIP/OM was maintained 9/1/0.1. The glass substrates were washed by regular washing (acetone, methanol, distilled water). The solution was vigourously stirred and deposited onto the glass substrates at 8000 rpm for 30 s. Subsequently, the resultant films were annealed at 550 °C for 15 hours [1, 2, 6]. Identification of phases of titania thin films was performed by X-Ray Diffraction (XRD, Advanced Brucker Diffractometer) and Raman spectroscopy (Renishaw Inva Raman Microscope). The optical features of the prepared samples were investigated by UV Visible (Jasco UV-Vis spectrophotometer).

3. Results and Discussion

3.1 Structural Studies

X-ray diffraction pattern has been used for the phase identification of as deposited and annealed at 550 °C nanocrystalline TiO_2 thin films onto the glass substrate. The diffraction patterns of as prepared films do not show any peak (Figure 1a) due to low crystallinity, which indicates that the films have amorphous nature [11]. The peaks located at 2θ of about 25.1, 48.3, 63.1, and 70.1 correspond to the Miller indices of (101), (200), (204), and (116) planes respectively. These peaks exhibit the formation of pure anatase phase for the post-annealed film at 550 °C (Figure 1(b)). The nucleation and growth of grains and increase in crystallinity are conspicuously observed for these films [2, 4, 10]. The results of XRD patterns are in good jibe to the standard JCPDS data of anatase phase of TiO_2. Scherrer equation has been used to calculate the crystallite size of titania thin films and results showed 18-22 nm particles sizes.

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{3.1}$$

where, D is the average crystallite size, λ is the wavelength of the X-ray radiation (Cu Kα = 0.15418 nm), β is the full width at half-maximum height, and θ is the Bragg diffraction angle [3]. The rise in the particle size after heat treatment could be owing to the agglomeration and re-crystallization of titania films at higher temperature [1–5].

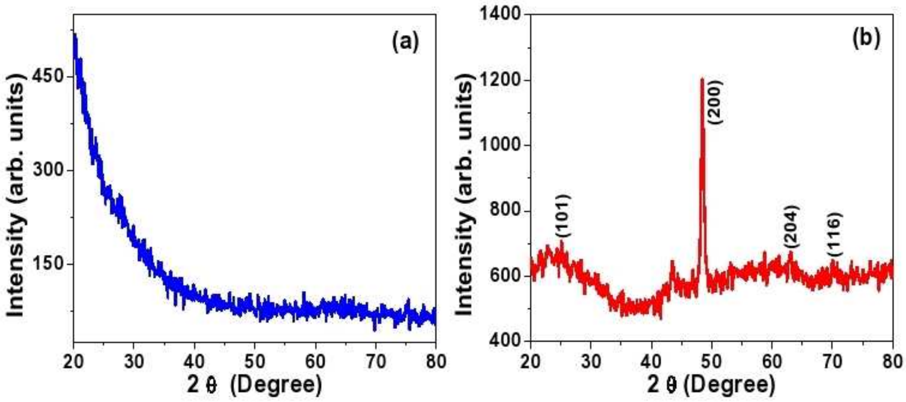

Figure 1. XRD patterns of (a) as deposited and (b) annealed at 550 °C TiO_2 thin films.

3.2 Raman Spectroscopy

The results of XRD were confirmed using Raman spectroscopy. Figure 2 demonstrates the Raman spectra recorded at room temperature with excitation wavelength 532 nm line of an Argon ion laser as the source in the range of 100-800 cm^{-1} on as prepared and annealed titania thin films at 550 °C.

Figure 2(a) shows no peak, suggesting the amorphous nature of as prepared film. As it is depicted in the Figure 2(b), three active modes at, 144 cm^{-1}, 458 cm^{-1}, and 561 cm^{-1}, are identified as the anatase phase of titania for samples annealed at 550 °C. The locations of bands are in good agreement with previous reports for anatase phase and no rutile traces were observed in the samples. Hence, the results of XRD are complimented by Raman spectroscopy studies, which showed the expected vibrational modes of anatase TiO_2 [1].

3.3 Optical Properties

Figure 3(a), (b) show the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ and Figure 3(c), (d) depict the transmission spectra of as synthesized and calcinated at 550 °C nanocrystalline TiO_2 thin films. The absorption edges are found to be 380 and 385 nm for as deposited and annealed samples at 550 °C respectively. There is a red shift (slight shift towards longer wavelength side) in the absorption wavelength which is related to the increase in particle size after heat treatment [1,3].

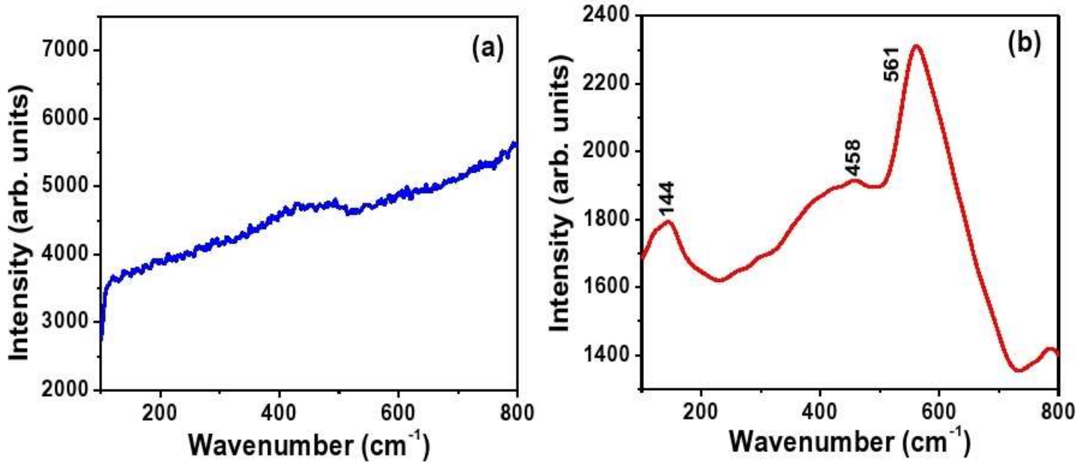

Figure 2. Raman patterns of (a) as deposited and (b) annealed at 550 °C TiO_2 thin films.

The energy band gap (E_g) of the films was evaluated from the direct transition of electrons from the top of the valance band to the bottom of the conduction band. The estimated energy band gap was 3.26 eV for as deposited sample, thereafter decreased to 3.22 eV for 550 °C annealed TiO_2 films.

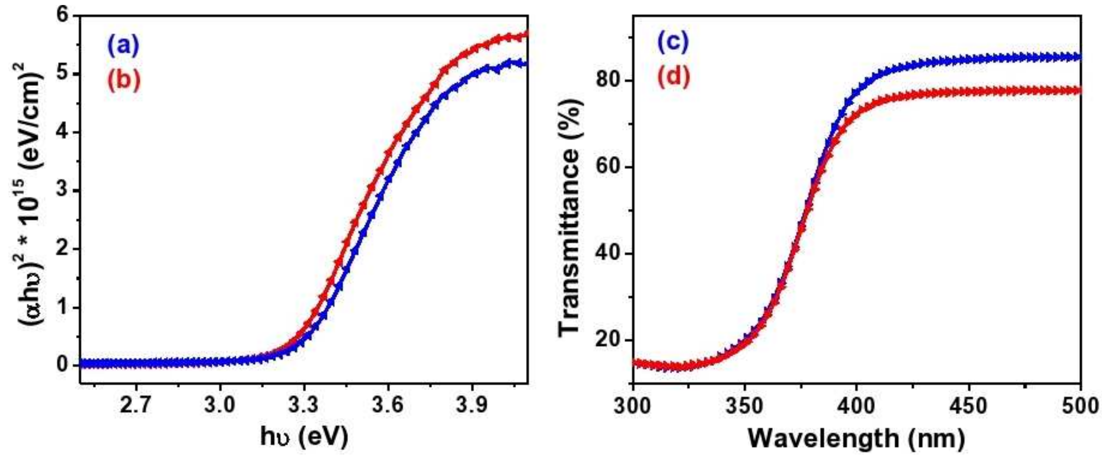

Figure 3. UV graphs of (a), (c) as prepared and (b), (d) annealed at 550 °C TiO_2 samples.

The decrease in the energy band gap upon increasing the calcination temperature could be due to increase in particle size and phase transformation from amorphous to anatase [1, 6]. The transmittance (%) spectra of the as-deposited and annealed films at 550 °C were about 86 and 77 % respectively. The change in transmittance is due to the increase in surface scattering which is related to the surface roughness [1–5].

The absorption coefficients (α) of the films were estimated from the transmission spectra (T) in the visible region using the following empirical expression [5, 10, 12]

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \tag{3.2}$$

where T is the maximum transmittance and t is the thickness of the film. The estimated absorption coefficients at a wavelength of 500 nm were $96.7 * 10^6\ \mathrm{m}^{-1}$ and $94.6 * 10^6\ \mathrm{m}^{-1}$ for as deposited and annealed titania thin film at 550 °C which conspicuously show a reduction trend after heat treatment. The relation between absorption coefficient (α) and the incident photon energy ($h\ \nu$) is given by

$$\alpha h\nu = A(h\nu - E_g)^n \tag{3.3}$$

where A is a constant, $h$is the Planck's constant, ν the frequency of incident radiation, E_g is the band gap of the material and n is equal to one for direct gap and four for indirect allowed transition. The optical band gap energy (E_g) has been also calculated using the above relation. The same values as obtained using the relation (3.2) have been achieved by applying expression (3.3). The band gap values have been also evaluated by drawing the straight peripheral line portion of the curve of $(\alpha h\nu)^2$ against ($h\nu$) horizontal axis [2, 11, 12].

4. Conclusions

In summary, we have successfully prepared nanostructured titania films using sol-gel dip coating method. The effect of post-heat treatment on the structural and optical properties of TiO_2 films was studied. The results of XRD confirmed the amorphous nature for as synthesized and anatase phase for sintered sample at 550 °C. These results were further confirmed using Raman spectroscopy. The post annealing is found to have a remarkably affect on the properties of TiO_2 thin films. The crystallite size was increased and the optical study revealed a red shift in the absorption edge and decrease in the energy band gap and transmission spectra after heat treatment. The former was attributed to the improvement in the crystal structures of titania thin films and the later was owing to either change in particle size and phase transformation from amorphous to anatase.

Competing Interests

The author declare that he has no competing interests.

Authors' Contributions

The author read and approved the final manuscript.

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