Effect of molarity on sol-gel routed nano TiO₂ thin films

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The nanostructured titanium dioxide (TiO₂) thin films have been prepared for the molar concentrations of titanium tetra isopropoxide (TTIP) 0.05 M, 0.1 M, 0.15 M and 0.2 M by sol-gel routed spin coating technique with calcination at 450°C. The processing parameters such as, pH value (8), catalyst HCl (0.1 ml), spin speed (3000 rpm) and calcination temperature (450°C) are optimized. The crystalline nature and surface morphology were analyzed by XRD, SEM and AFM analysis. The XRD results confirm that the films are crystalline with anatase phase, and are nanostructured. The SEM micrographs of the TiO₂ film reveal the spherical nature of the particle. AFM analysis establishes that the uniformity of the TiO₂ thin film was optimized at 0.2 M. The optical measurements show that the transmittance depends on the molarity, and the optical band gap energy of TiO₂ films is found to be inversely proportional to molarity. The I-V characteristics exhibit that the molarity strongly influences the electrical conductivity of the film. The results indicate that the significant effect of molarity on structural, optical and electrical properties of the nanostructured TiO₂ thin films will be useful to photovoltaic application.

Keywords: TiO₂ thin film; titanium tetra isopropoxide; sol-gel; precursor concentration; calcination temperature.

1. Introduction

Nanocrystalline titanium dioxide (TiO₂) films are extensively studied because of their interesting chemical, electrical and optical properties. TiO₂ is one of the most important transition metal oxide semiconductor with wide band gap which is suitable for solar energy conversion applications such as antireflection coatings for photovoltaic cells and passive solar collectors,^{1,2} photochromic,³ dye-sensitized nanocrystalline solar cells,^{4,5} and photo-catalysis,⁶ and gas sensors.⁷

A wide variety of techniques have been used to prepare titania films, and these include chemical vapor deposition (CVD),⁸ pulsed laser deposition, reactive sputtering,⁹ and sol-gel deposition.¹⁰ The sol-gel technique has emerged as one of the most promising methods as it produces samples by simple synthetic route with good homogeneity, low cost, excellent compositional control and feasibility of producing thin films on large complex shapes with low crystallization temperature.

The properties of TiO₂ films depend not only on the preparation technique, but also on the deposition conditions that determine the nucleation and growth of the crystal phase.¹¹ The preparation of the nano TiO₂ thin films and its influences in structural, optical and electrical properties have been investigated by many research groups. In sol-gel synthesis, the formation of thin films depends on parameters like sol reactivity, viscosity, water alkoxide ratio and metal precursor concentration. Hence, TiO₂ thin films with the desired

properties can be obtained in this technique by optimizing the various processing parameters like viscosity of sol, pH of solution, catalyst, spin speed and calcination temperature. There are many works carried out on the crystalline property, and the formation of nanostructured thin films depend mainly on the molar concentration of the precursor.¹² Temperature also plays an important role in the formation of TiO₂ thin films, as it determines the nucleation and growth of nanostructures.¹³ There are few works were carried out on the influence of molarity on the TiO₂ thin films and study the effects on structural, optical and electrical properties of films with optimized conditions.

The novelty of the present work is the optimization of the processing parameters pH value (8), amount of catalyst (HCl), spin speed (3000 rpm) and calcination temperature (450°C) for the preparation of sol-gel routed spin coated nano TiO₂ thin films with molar concentrations 0.05 M, 0.1 M, 0.15 M and 0.2 M and also the study of the effect of molarity on its structural, optical and electrical behaviors useful to photovoltaic applications.

2. Experiment

2.1. Materials

The precursors used in the preparation of nano TiO₂ film by sol-gel technique were: titanium tetra isopropoxide

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(TTIP, 98%), isopropanol (98%) and hydrochloric acid (97%) from Sigma Aldrich Co. Ltd. The glass plate is used as a substrate.

2.2. TiO_2 film preparation

TTIP was used as a precursor, hydrochloric acid as a chelating agent, isopropanol and deionized water as a solvent. Triton X-100 was used as a stabilizer to avoid precipitation in solution and at the same time used to increase the conductivity of films. TTIP (3.5 ml) was slowly added to the mixture of isopropanol (25 ml), concentric hydrochloric acid (0.1 ml, catalyst) and distilled water (0.2 ml) with constant stirring for 30 min. Introduction of isopropanol prior to TTIP induces immediate precipitation due to highly reactive alkoxide, therefore Triton X-100 was added as a stabilizing agent for the hydrolysis reaction. The resultant alkoxide solution was kept at room temperature for hydrolysis reaction for 2 h, resulting in a transparent pale yellowish TiO_2 sol. The hydrolysis and the poly condensation of titanium alkoxides proceeds according to the following mechanism¹⁴:

TiO_2 sol was deposited on to a glass substrate by a spin coating unit with spin rate at 3000 rpm for 60 s in air and dried on a hot plate at 100°C for 60 s. The prepared samples

Fig. 1. Flow diagram for preparation of TiO_2 thin films through sol-gel routed spin-coating method.

were calcinated at 450°C for 1 h. Figure 1 shows the flow chart of the processing of the sol-gel routed TiO_2 thin films using the spin coating technique.

2.3. Characterization of TiO_2 film

The XRD patterns were obtained for identifying the crystal phase with a XPERT-PRO X-ray diffractometer with $\text{Cu K}\alpha$ radiation in the range of 2θ values from 20° to 80° ($\lambda = 0.1540 \text{ nm}$). The structural characteristics of TiO_2 films were analyzed by the VEGA3 TESCAN scanning electron microscope and atomic force microscope (AFM XE-100). The properties of the films deposited on glass substrates were examined with the normal incident transmittance measured by a UV-VIS spectrophotometer (Lambda 35 UV-Vis (Perkin Elmer)). Four probe techniques were used to investigate the electrical properties of TiO_2 films.

3. Result and Discussion

3.1. X-ray diffraction analysis

The phase composition and the crystallite size of the prepared TiO_2 films were evaluated by X-ray diffraction analysis. Figure 2 illustrates the XRD pattern of TiO_2 films of different molar concentrations of TTIP deposited at room temperature and calcined at 450°C . The diffraction pattern indicates the crystalline nature of the films having anatase phase only. The characteristic peaks corresponding to 2θ values 25° , 37° , 48° , 53° and 62° are (101), (004), (200), (105) and (204), respectively. The intensity of (101) peak corresponds to the anatase phase decreases progressively as increase in precursor concentration. This leads to broad nature of diffraction peak and the smaller size of the particles.¹⁵ The crystalline nature (tetragonal) and purity of the sample are confirmed by comparing the data with JCPDS (Card No: 21-1272) data.¹⁶

Fig. 2. XRD pattern of TiO_2 films prepared for TTIP concentrations 0.05, 0.1, 0.15 and 0.2 M.

Table 1. Effect of molarity on TiO₂ thin film.

Sample	Molarity	Crystallite size (nm)	Thickness (nm)
1	0.05 M	27.6	29.3
2	0.10 M	24.2	34.6
3	0.15 M	16.5	59.2
4	0.20 M	7.7	62.4

The crystallinity (anatase) of TiO₂ particles is gradually maintained with the temperature up to 450°C. With further increase of temperature, the primary particles began to aggregate to form secondary larger particles. Thus, 450°C is considered to be the optimum temperature for the anatase phase.^{17–19}

The crystallite size was obtained from Debye–Scherrer's formula²⁰:

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (2)$$

where D is the crystallite size (nm), λ is the wavelength of X-ray radiation ($\lambda = 0.154$ nm) for Cu K_{α} , K is the

coefficient (0.89), β is full width half maximum FWHM intensity (radian) and θ is the corresponding diffraction angle.^{21,22}

From XRD analysis, the crystallite size of TiO₂ nanoparticles gradually decreases with increase of molarity. The thickness of TiO₂ film increases with the increase in molarity as in Table 1. The crystallite size of TiO₂ greatly depends on the precursor concentration. There is a greater number of nanosized TiO₂ nuclei evolved under the higher concentration of TTIP during the hydrothermal reaction at lower temperature.^{23,24}

3.2. Surface morphological analysis

3.2.1. Scanning electron microscopy analysis

The SEM micrographs (Fig. 3) of nano TiO₂ films prepared for 0.05 M and 0.2 M molar concentrations of TTIP calcined at 450°C exhibit that the crystallite sizes of the particles increases with the increase of molar concentration. This result indicates that the higher concentration of solute particles leads to agglomeration. The XRD result confirms that the size

Fig. 3. The SEM micrographs of (a) 0.05 M and (b) 0.2 M TiO₂ films calcined at 450°C.

Fig. 4. AFM images of (a) planar view and (b) 3D view of TiO₂ thin films for 0.05 M. Fig. 5. AFM images of (a) planar view and (b) 3D view of TiO₂ thin films for 0.2 M.

of the TiO₂ particles are in the nanometric range. The SEM images of TiO₂ films reveal the formation of less densified nanosized TiO₂ particles.^{23,25}

3.2.2. Atomic force microscopy analysis

The topography images of TiO₂ Figs. 4 and 5 in tapping mode confirm the uniform distribution of spherical-shaped particles. The average roughness values of the TiO₂ films were found to be 15.4 nm, 18.3 nm, 21.6 nm and 27.8 nm with the increase of molarity. The TiO₂ thin film of 0.2 M exhibits good uniformity compared to the other films and the roughness of TiO₂ films depends on the molarity due to the particle size.¹²

4. Optical Analysis

The UV–Vis optical absorbance and transmittance spectra of TiO₂ films prepared for different molar concentrations 0.05, 0.1, 0.15 and 0.2 M and calcined at 450°C are shown in Figs. 6(a) and 6(b). The absorbance spectrum of the prepared TiO₂ films shows that the increase of molarity improves the

absorbance behavior of TiO₂ films due to the high density of TiO₂ particles. Hence, the higher absorption value in the visible region reveals that a large amount of photon energy will be absorbed resulting in more excitation of electrons into the conduction band of TiO₂.²⁶

The transmission spectra of TiO₂ thin films, Fig. 6, for different molar concentrations of precursor 0.05 M, 0.1 M, 0.15 M and 0.2 M exhibits high transparency in the visible range of 400–900 nm. The refractive index of the TiO₂ thin films prepared from different molar concentrations of the precursor (0.05, 0.1, 0.15 and 0.2 M) were calculated from the transmittance spectrum.

The refractive index $n(\lambda)$ over the spectral range is calculated using the relation

$$n(\lambda) = \sqrt{S + \sqrt{S^2 - n_0^2(\lambda)n_s^2(\lambda)}}, \quad (3)$$

$$S = \frac{1}{2}n_0^2(\lambda) + n_s^2(\lambda) + 2n_0n_s \frac{T_{\max}(\lambda) - T_{\min}(\lambda)}{T_{\max}(\lambda)T_{\min}(\lambda)}, \quad (4)$$

where n_0 is the refractive index of air, n is the refractive index of the substrate, $T_{\max}$ is the maximum envelope and $T_{\min}$ is the minimum envelope. The refractive index and porosity of

Fig. 6. The UV-Vis optical (a) absorbance spectra and (b) transmittance spectra of TiO₂ films calcined at 450°C.

Table 2. Effect of molarity on optical property of TiO₂ thin films.

Molarity of sample	Refractive index	Porosity (%)	Optical band gap energy (eV)
0.05 M	2.15	34.16	4.15
0.1 M	2.21	29.41	3.95
0.15 M	2.34	18.6	3.82
0.2 M	2.45	9.1	3.75

TiO₂ thin films prepared from different molar concentrations are listed in Table 2. It is seen that the refractive index of the prepared TiO₂ films has the average value of 2.28.

The porosity of the thin films is calculated using the following equation²⁷:

$$\text{Porosity} = \left(1 - \frac{n^2 - 1}{n_d^2 - 1}\right) \times 100\%, \quad (5)$$

where n_d is the refractive index of pore-free anatase ($n_d = 2.52$),²⁸ and n is the refractive index of the porous thin

films. The porosity of the TiO₂ film decreases with increase of molar concentration due to densification and pore destruction in films during calcination.

The optical band gap energy (E_g) of TiO₂ films are obtained from the direct transition of electrons between the edges of the valence band and the conduction band. From the extrapolation of the graph in Fig. 7, the band gap energy for 0.05 M and 0.2 M are 4.15 eV and 3.75 eV, respectively. The value of the optical band gap energy decreases with the increase of the molarity.

5. Electrical Analysis

The current-voltage (I - V) characteristics of the TiO₂ thin film for the molarity 0.05 M and 0.2 M are shown in Fig. 8. The current-voltage measurement has been carried out for TiO₂ films using the four probe techniques. The resistance of the TiO₂ film was determined using the relation^{29,30}

$$R = \rho \left(\frac{L}{A} \right), \quad (6)$$

Fig. 7. Optical band gap energy of TiO₂ thin films calcined at 450°C.

Fig. 8. The current-voltage characteristics of TiO₂ thin film.

Fig. 9. Conductivity of TiO₂ thin film with different molarities.

where L and A are the length and area of cross-section of the contact probe, respectively. The electrical conductivity obtained using the relation film was determined using the relation³¹

$$\sigma = \frac{1}{\rho}. \quad (7)$$

From the I - V characteristics, the saturation current of TiO₂ thin film is found to be 1.8×10^{-8} A for 0.2 M concentration and 1.6×10^{-8} A for 0.05 M concentration. The electrical conductivity of TiO₂ thin films with different molar concentrations are shown in Fig. 9. Thus, the conductivity of TiO₂ film increases with the increase of molarity due to increase in the electron carrier concentration at the higher density of TiO₂.^{31,32}

6. Conclusion

The nanostructured titanium dioxide (TiO₂) thin films were prepared using the sol-gel routed spin coating technique. TiO₂ thin films are crystallized as anatase phase and are nanostructured with the tetragonal system. The SEM images exhibit that the particles are spherical in nature. TiO₂ thin film prepared at 0.2 M concentration has a smooth surface. The roughness of the TiO₂ thin film increases with the increase of molarity. The optical transmittance is found to depend on the molarity and the higher value of molarity leads to lower optical band gap energy. The molarity strongly influences the electrical conductivity of TiO₂ film. Hence, the nano TiO₂ thin films with higher molar concentration will be useful for photovoltaic applications due to their structural, optical and electrical behaviors.

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