Enhancement of Photovoltaic Properties of Dye Sensitized Solar Cell using Nanocrystalline TiO_2 Films

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Abstract

Nanocrystalline TiO_2 films are prepared by using two steps processing - (i) sol-gel dip-coating at room temperature and (ii) annealing at 300, 400 and 500 ^0C for 2 hr. The films are characterized by X-ray diffraction (XRD), Raman spectroscopy, Scanning electron microscopy (SEM) and UV-Visible spectroscopy. The characterization studies using XRD and Raman spectra showed the formation of pure anatase TiO_2 in annealed films with average crystallite size ~ 18 nm. UV-visible spectra showed increase % transmittance and absorption coefficient with increasing the annealing temperature. The better photovoltaic performance: open circuit voltage = 0.714 V, current density = 0.59 mA/cm^2, fill factor = 38.66 % and efficiency = 0.163 % by using polyiodide electrolyte is obtained for Rose Bengal dye sensitized solar cells of TiO_2 films having thickness ~ 972 nm and annealed at 500 ^0C for 2h.

Keywords: Nanocrystalline; Anatase TiO_2; Films; Optical properties; Dye sensitized solar cell.

Introduction

In modern day research, wide band gap semiconductors are focused materials due to their potential applications in many areas, such as sensors, laser diodes and other high speed electronic devices [1-3]. TiO_2 has attracted considerable attention owing to its wide band gap [4]. Thin films of TiO_2 has been studied widely in recent years because of its suitability for many applications like environmental applications [5], photocatalysis [6], electrochromic devices and photovoltaic cells [7] because of its biocompatibility, thermal stability, strong oxidized stability, non-toxicity and long term photo-stability. It is also a material, which is being used in non-electronic applications like optical brightener in wall colors, ingredient in sun cream and bone implants [8]. TiO_2 thin films have been deposited in the past by many researchers by using different techniques like, molecular beam epitaxial growth, chemical vapor deposition, aerosol pyrolysis, electrodeposition and sol-gel method [9-10]. Out of these methods, the sol–gel method is simple, inexpensive, non-vacuum and low temperature technique for preparation films. In the present study, TiO_2 films with anatase phase are prepared by using titanium tetra isopropoxide by the simple sol-gel dip-coating method at room temperature. This resultant TiO_2 films as photoelectrode are used for the fabrication of DSSCs with Rose Bengal dye. An attempt is made to enhance photovoltaic properties of anatase phase TiO_2 films after annealing.

Experimental Work

Material and Methods

Titanium tetra isopropoxide (TTIP) was used as the titanium precursor. The matrix sol was prepared by mixing TTIP with absolute ethanol and acetic acid at room temperature (RT). Here, absolute ethanol was used as solvent. Further, acetic acid was used as catalyst to control the pH of hydrolysis/condensation reaction in the sol-gel solution. The mixture solution was stirred for about 1 hr. In mixture, the molar ratio of precursor, solvent and catalyst was TTIP: ethanol: acetic acid = 0.05:0.5:0.1. The films were coated onto well cleaned indium tin oxide (ITO) substrates using by dipping the substrates in above mentioned mixture solution. The coated films were heated at 100 ^{0}C in air for 10 min. and then allowed to cool to RT naturally. The dip-coating, heating and cooling process was repeated for five times in order to get thicker films. The heating of the film after each deposition was carried out to enhance the stabilization of the meso-phases involved. The films were annealed at 300, 400 and 500 ^{0}C for 2 hr. X-ray diffraction patterns were recorded by using Bruker D8 Advance (filtered CuK_α radiation, λ = 1.5406 Å) machine. Raman spectra were recorded by Jobin Yvon Horibra LABRAM-HR (single mode Ar-ion laser for excitation λ = 488 nm) spectrometer. Thickness of the films was measured by using surface profiler (KLA Tencor P -16+). The optical spectra of resultant films were recorded by using the UV-Visible spectrophotometer (V-670, JASCO UV-VIS-NIR spectrometer). Surface morphology was determined by using scanning electron microscope (JEOL JSM-6360-LA and Philips XL-30).

Fabrication of DSSCs

The films heated at 300, 400 and 500 ^{0}C were used for dye sensitized solar cell application. This film was immersed in a 0.3 mM solution of Rose Bengal dye for 24 hr. Then film was rinsed with acetonitrile to remove excess amount of dye and dried at room temperature. One drop of an iodine-based electrolyte solution was deposited onto the surface of this film. This film deposited with dye was further used as working electrode. The carbon coated ITO substrate was used as counter electrode. The counter electrode was clamped on the top of working electrode to form DSSC. The black and red wires with alligator clips were connected to negative working electrode and positive counter electrode respectively. The current density (J)- voltage (V) characteristic curves for different DSSCs (area = 0.25 cm^2) recorded at the input power = 1000 W/m^2 of incident light from neon lamp by using solar simulator (Newport Corporation's Oriel® Sol2A® Class ABA solar simulation systems) to obtain the photovoltaic properties of DSSCs.

Results and Discussions

X-ray diffraction (XRD)

The X-ray diffraction patterns of films annealed at different temperatures are shown in Figure 1. The diffraction patterns display crystalline nature with simultaneous presence of broad hump in the low 2θ region demonstrating its short range ordering. The diffraction pattern of film annealed at 300 ^{0}C exhibit broad hump with only one peak indicating that the film is amorphous. The diffraction patterns of films annealed at 400 and 500 ^{0}C show distinct peaks with low intensities. The peaks are indexed and found to be that of anatase TiO_2. The peak at $2\theta = 25.3^o$ is the characteristic peak of anatase phase and corresponds to (101) direction. The diffraction peaks (004), (200) and (105) corresponding to the anatase TiO_2 phase is also observed in the X-ray diffraction pattern of 400 ^{0}C and 500 ^{0}C annealed films. No peaks corresponding to the rutile phase of TiO_2 are seen in the diffractogram suggesting clearly that only anatase phase is formed in resultant films. The peaks positions and their relative intensities are noted to be consistent with the standard powder diffraction pattern of anatase TiO_2. The crystallite size is determined from the integral width of the (101) plane using Scherer's formula [11] and is obtained for films annealed at 300, 400 and 500 ^{0}C.

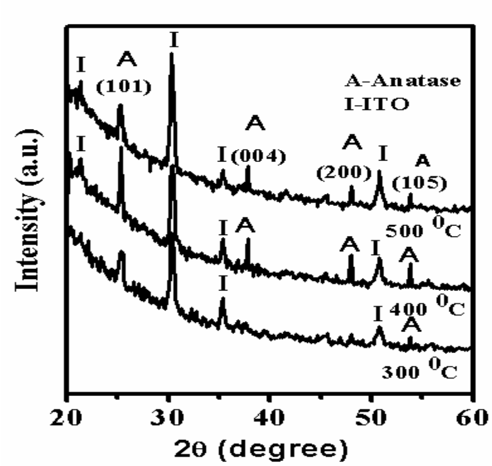


Figure 1. XRD patterns of resultant films

The crystallite size is found to be increasing with increasing annealing temperature. The annealing at higher temperature facilitates the subsequent crystal growth process, accompanied by the diffusion of titania species towards nucleated grains resulting in grain growth. The data for crystallite size, interplaner spacing d, lattice parameter (a = b and c) and unit cell volume for resultant TiO_2 films is summarized in Table 1. The data obtained for resultant films is found to matching with reported values.

Table 1. Structural properties of films annealed at different temperatures

Parameter		Annealing Temp. (^{0}C)		
		300	**400**	**500**
Crystallite size (nm)		16.48	18.71	19.02
d_{101} spacing	Obs.	0.3513	0.3518	0.3517
	Std	0.3520	0.3520	0.3520
Phase symmetry		Anatase	Anatase	Anatase
Lattice parameter	a	0.3781	0.3775	0.3781
	b	0.3781	0.3775	0.3781
	c	0.9499	0.9498	0.9499
Unit cell volume (nm)^3		0.1358	0.1354	0.1358

Obs. – Observed, Std. - Standard

Raman spectroscopy

The Raman spectra of the films annealed at 300, 400 and 500 ^{0}C are shown in Figure 2. The Raman spectra show well defined peaks and the absence of overlapping peaks confirming that the films are well crystallized with low number of imperfect sites. The anatase TiO_2 has six Raman active modes: A_{1g} + $2B_{1g}$ + $3E_g$. For anatase TiO_2 single crystal, Ohsaka et al. [12] have reported the following allowed bands: 142 ± 2 cm^{-1} (E_g), 194 ± 3 cm^{-1} (E_g), 393 ± 2 cm^{-1} (B_{1g}), 512 ± 1 cm^{-1} (A_{1g}), 519 ± 1 cm^{-1} (B_{1g}) and 634 ± 2 cm^{-1} (E_g). The five distinct peaks (Figure 2) are observed in the Raman spectra of all films, which can be assigned according to the above-given allowed modes of anatase TiO_2. The observed spectra have bands centered at 144.3 cm^{-1} (E_g), 195.8 cm^{-1} (E_g), 395.8 cm^{-1} (B_{1g}), 517.1 cm^{-1} (A_{1g}) and 635.7 cm^{-1} (E_g).

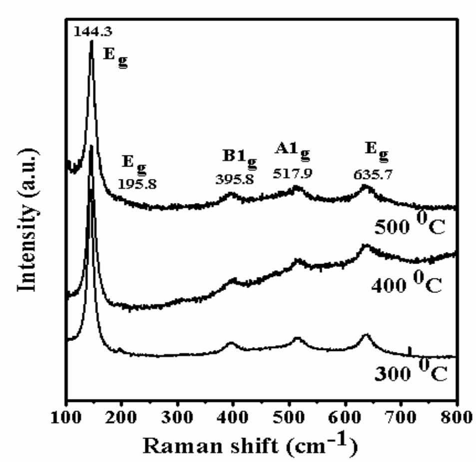
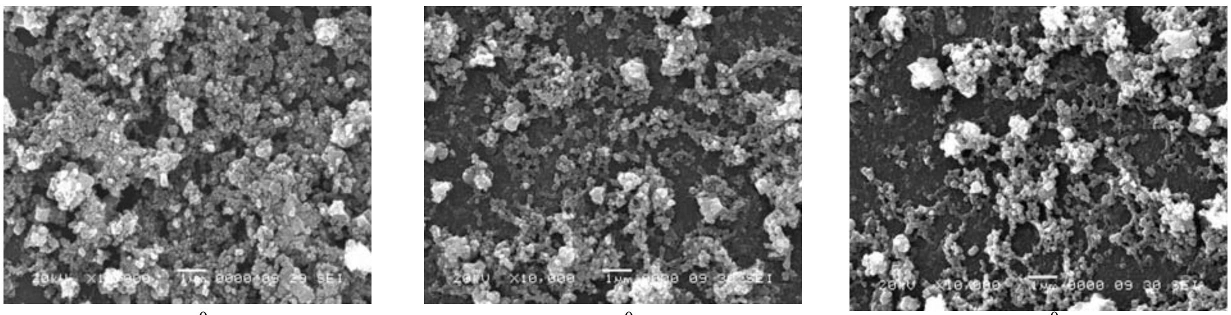


Figure 2. Raman spectra of films annealed at different temperatures

The absence of peaks corresponding to the rutile phase in the Raman spectra confirms the formation of pure anatase TiO_2. This statement agrees with the results obtained in literature [13] for TiO_2 films heated at 700 ^{0}C.

Scanning electron microscopy

For morphological analysis, coated TiO_2 film was peeled out from the substrate and subjected to scanning electron microscopy (SEM) analysis. The SEM images of sol-gel dip-coated films annealed at 300, 400 and 500 ^{0}C are shown in Figure 3.



300 ^{0}C 400 ^{0}C 500 ^{0}C

Figure 3. SEM images for films annealed at different temperatures

The SEM images for films annealed at different temperatures show the following observations: (i) primary particles are nearly spherical, (ii) particle size distribution of primary particles is nearly uniform and (iii) nature of particles is soft/hard agglomerates. The agglomerates also show varied morphology at higher annealing temperature.

Optical band gap

Figure 3 (a) gives the UV-Visible transmittance spectra for the films annealed different temperatures. The Tauc's plots [14] generated from the UV-Visible spectra for the films annealed different temperatures are given in the Figure 4 (b) to obtain the band gap energy (E_g).

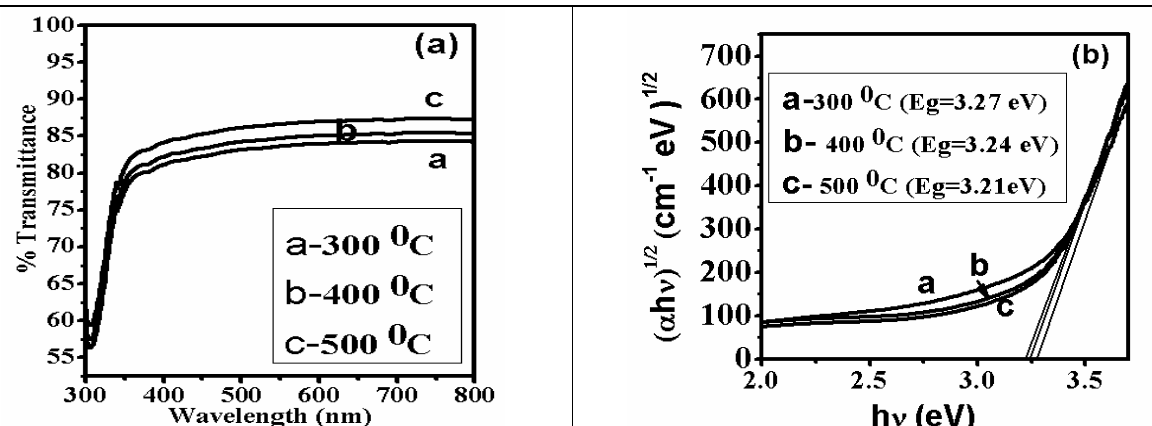


Figure 4. (a) UV- Visible transmittance spectra, and (b) variation of $(\alpha h\nu)^{1/2}$ vs. hν (indirect band gap) for films annealed at different temperatures

The value of indirect band gap energy E_g is obtained by extrapolation of straight-line portion of the plot to zero absorption edge. Further, the absorption coefficient is obtained by using relation,

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \quad \text{--- (1)}$$

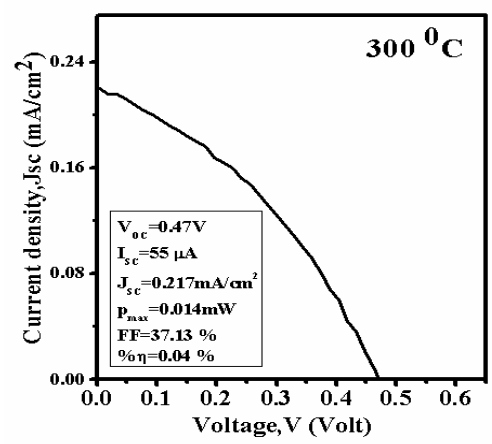
where, d = thickness of film, and T = % transmittance of film. The optical properties of films annealed at different temperatures are given in Table 2. The thickness of the films is seen to be decreasing at higher annealing temperature. This is due to densification of film at higher annealing temperature. Further, due to decreasing thickness the transmittance and absorption coefficient are also found to increasing with the annealing temperature.

Table 2. Optical properties of films at different temperatures

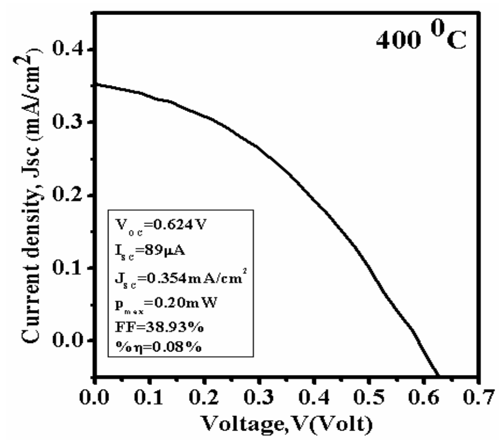
Temperature (^{0}C)	d (nm)	% T at λ = 550 nm	Indirect band gap, E_g eV	Absorption coefficient (α) x 10^4 (cm^{-1})
300	687	83	3.27	0.12
400	679	85	3.24	0.13
500	672	87	3.21	0.15

Photovoltaic properties

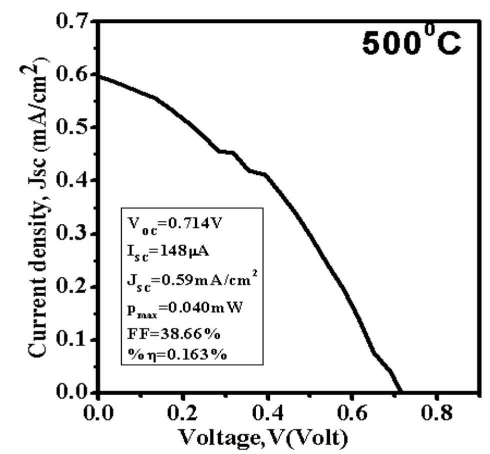
The films annealed at different temperatures were used for dye sensitized solar cell characteristics study. The cell under test was illuminated under standard AM 1.5 simulated sunlight (power density of 1000 W/cm^2). The solar cell J - V curves were recorded for given cell immediately after its fabrication. Figure 5 shows the current density versus voltage curves for the DSSCs made with photoanodes of films annealed at different temperatures. The solar cell characteristics obtained for different DSSCs are summarized in Table 3. All the data as compared to reported data, which might be good for Rose Bengal dye. The better performance of these solar cells might be due to the lower stability of Rose Bengal under the ambient surroundings.



(a)



(b)



(c)

Figure 5. Current density versus voltage curves for DSSCs made with photoanodes of films annealed at different temperatures

Table 3. Photovoltaic properties for DSSCs made with photoanodes of films annealed at different temperatures

DSSC Parameter	Annealing Temp. (^{0}C)		
	300	400	500
Thickness, d (nm)	687	679	672
Open circuit voltage, V_{OC} (volt)	0.47	0.624	0.714
Short circuit current, I_{SC} (μA)	55	89	148
Maximum voltage, V_{MAX} (volt)	0.271	0.400	0.405
Maximum current, I_{MAX} (μA)	35	66	101
Maximum power, P_{MAX} (mW)	0.014	0.023	0.040
Current density, J_{SC} (mA/cm^2)	0.217	0.354	0.590
Fill Factor, FF (%)	37.13	38.93	38.66
Efficiency, n (%)	0.04	0.08	0.163
Series resistance, R_S (Ω)	2464.1	2537.5	1154.1
Shunt resistance, R_{SH} (kΩ)	141.76	53.63	39.782

Conclusions

The sol-gel dip-coating is simple, cheap and versatile processing route useful for the preparation of nanocrystalline anatase TiO_2 films. The structural and morphological studies of resultant films confirmed the phase pure nanocrystalline state of materials of TiO_2 films. The optical properties are found to be influenced by annealing temperature. These films might be having good potential for application like photoelectrode for dye sensitized solar cells.

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