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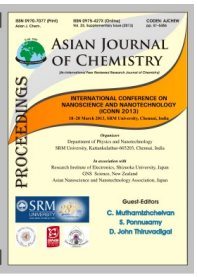

Effect of Thickness and Dye on Optical and Photovoltaic Properties of Nanocrystalline TiO_2 Thin Film for Dye Sensitized Solar Cell Application†

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Different thickness of dye sensitized solar cells of TiO_2 thin films prepared by modified sol-gel method with Eosin-Y and Rose Bengal dyes are investigated in present communication. As deposited films 1, 3 and 5 layer coating were annealed 400 ºC/2 h. The resultant films were characterized by using XRD, Raman spectroscopy, SEM, TEM and UV-visible spectroscopy. The structural studies revealed the evolution of pure anatase TiO_2 phase in resultant films. The morphological studies with SEM indicated nearly uniform size distribution of spherical agglomerates in resultant films. The TEM studies indicated nanocrystalline state of films (average particle size ~ 25 nm) consistent with XRD results of crystallite size = 20-30 nm. The better optical properties: indirect band gap energy, absorbance coefficient, transmittance, refractive index and porosity ratio are 3.22 eV, 2.8×10^4 cm^{-1}, 86 %, 2.02 and 43.50 % respectively of the 5 layer coating film annealed at 400 ºC/2 h. The better photovoltaic performance: V_{OC} = 0.70 V, J_{SC} = 1.82 mA/cm^2, FF = 68.3 % and η = 0.87 % using Eosin-Y dye with polyiodide electrolyte are obtained for the dye sensitized solar cells of TiO_2 films generated from 5 layer coated film annealed at 400 ºC/2 h. The conversion efficiency increases with increasing thickness of film and it is greater for Eosin-Y than Rose Bengal dye.

Key Words: TiO_2 film, Sol-gel, Nanocrystalline, Dye sensitized solar cell, Eosin-Y, Rose Bengal dye.

INTRODUCTION

Recently, nanocrystalline semiconductor TiO_2 has been extensively studied in many applications due to its excellent physical, chemical, optical and photovoltaic properties[1-3]. The dye-sensitized solar cell consists of sensitizing dye, nanoporous metal oxide film, electrolyte and counter electrode. The metal oxide film plays a key role in the enhancement of photoelectric conversion efficiency (η) of dye sensitized solar cell. Many studies focus on the relation between film structure and photocatalytic activity-power conversion efficiency of dye sensitized solar cell[4,5]. A high incident photon to current conversion efficiency can be expected for TiO_2 films with better crystallization and higher specific surface area[6,7]. Among many deposition methods reported[8-10] for the preparation TiO_2 films, the sol-gel method has drawn a considerable amount of attention in scientific-technological area because of its advantages like low temperature processing, easy composition control and homogeneity and easy thin films fabrication with large area and low cost[11-13]. In this paper, we report the preparation of pure nanocrystalline-TiO_2 films on indium tin oxide (ITO)-coated glass substrates by using a sol-gel dip coating method. The effect of film thickness and dye used on optical and photovoltaic properties of nanocrystalline-TiO_2 films was investigated respectively.

EXPERIMENTAL

Titanium tetra-isopropoxide (Spectrochem. Chem.), isopropyl alcohol (Thomas Baker) and indium tin oxide coated glass (Aldrich Chem.) were used in the work of deposition of TiO_2 films. The materials: Eosin-Y and Rose bengal dyes [HIMEDIA], potassium hydroxide, potassium iodide, iodine and actonitrile (Thomas Baker) were used in dye sensitized solar cell fabrication of TiO_2 film.

A 1.7 mL of titanium tetra-isopropoxide was slowly added into 25 mL of isopropyl alcohol under vigorous stirring at room temperature for 1 h. Then it was aged for 4 h at rest to obtain the viscous sol. The thoroughly cleaned[12] indium tin

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oxide substrate and one side masked with tisco tape was dipped vertically into viscous sol for 1 min. and then pulled out with rate of 1-2 mm/sec to deposit film. Due to this thin liquid film stuck on exposed surface of substrate, hydrolyze rapidly with air humidity, and polycondensate leading to gel films. This film was dried (i) for 30 min in air to produce film-substrate chemical bond and then in an oven at 100 ºC/5 min. This process was repeated for 5 times to produce single layer of film. The films produced with 1, 3 and 5 layers and annealed at 400 ºC/ 2 h were identified as resultant films IM105, IM305 and IM505 respectively. In fabrication of dye sensitized solar cell, the resultant film was initially kept in 0.3 mM solution of Eosin-Y/Rose Bengal dye in ethanol at room temperature for 24 h, then rinsed with double distilled water and ethanol and finally dried gently in tissue paper. The carbon-coated side of ITO counter electrode was placed on the top of film. This assembly was used as dye sensitized solar cell. The few drops of electrolyte solution of polyiodide (1M KOH + 1M KI + 0.5 M iodine) in acetonitrile were poured from exposed side of dye sensitized solar cell. The dye sensitized solar cell's were made for all the films.

The X-ray diffraction patterns and Raman spectra recorded by using Bruker D_8 Advance (CuK_α radiation, λ = 1.5406 Å) diffractometer and Jobin Yvon Horibra LABRAM-HR spectrometer respectively were used for phase analysis of resultant films. The surface profiler [KLA Tencor P-16$^+$] was used to obtain thickness of films. The surface morphological study of films was done by using scanning electron microscopy (SEM) [Model JEOLJSM 6360, 20 kV] and transmission electron microscopy (TEM) [Model TECNAI G^2-20-TWIN, FEINETHRLANDS]. Micrograph TIA software was used to obtain interplanar distance from TEM image. The UV-visible spectra recorded by using V-670, JASCO spectrometer were used to obtain optical properties: transmittance (T %), absorption coefficient (α), band gap (E_g), refractive index (n), optical conductivity (σ_{opt}) and porosity (P %) of films. The I-V curves recorded for different dye sensitized solar cells (area = 0.25 cm^2) at input power = 1000 W/m^2 of incident light from neon lamp by using solar simulator [Newport Corpn., Oriel® Sol2A® class ABA] were used to obtain the photovoltaic properties: V_{OC}, I_{SC}, V_{max}, I_{max}, P_{max}, FF and η of different dye sensitized solar cell.

RESULTS AND DISCUSSION

Fig. 1 gives the XRD patterns for resultant films. The intensities of all the peaks in the XRD pattern for IM105 film are very small. This might be due to lower thickness of single layer coated IM105 film. Further, all the reflections in 3 XRD patterns are found to be matching with the peaks for pure anatase TiO_2 (JCPDS file No. 21-1272) only indicating thereby the formation of single phase material in all films. The peaks due to indium tin oxide substrate are marked by 'I'.

The values for average crystallite size (D) obtained by using Scherer's relation: $D = \frac{0.89\lambda}{\beta \cos\theta}$ [λ = 0.1541 nm, β = fwhm, θ = diffraction angle] are noted to be 22.86, 23.67 and 24.47 nm for IM105, IM305 and IM505 films respectively. The average values of (i) lattice parameters: a = b = 0.3787 nm, c = 0.9502 nm and (ii) d_{101} spacing = 0.3513 nm obtained

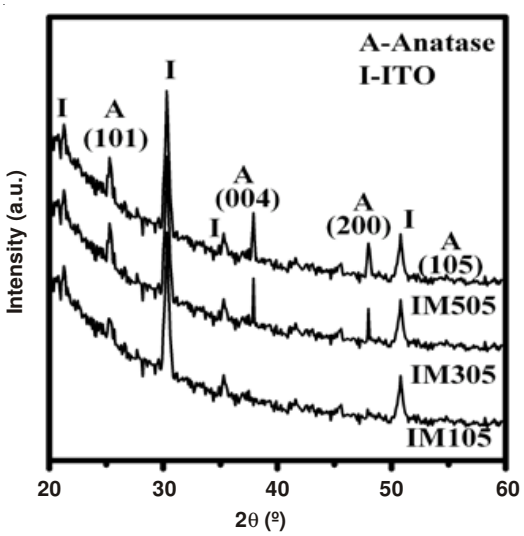

Fig. 1. XRD patterns for resultant films

for these films are found be to matching with respective data given in literature[14] for TiO_2 films (a = b = 0.3730 nm, c = 0.9485 nm and d = 0.3520 nm). Fig. 2 gives the Raman spectra for resultant films. All the spectra show (i) well defined peaks, (ii) absence of overlapping peaks and (iii) the peaks without any shoulders. These observations indicate the (i) formation of single phase materials and (ii) well crystallized nature with low number of imperfect sites in all films. All spectra show 5

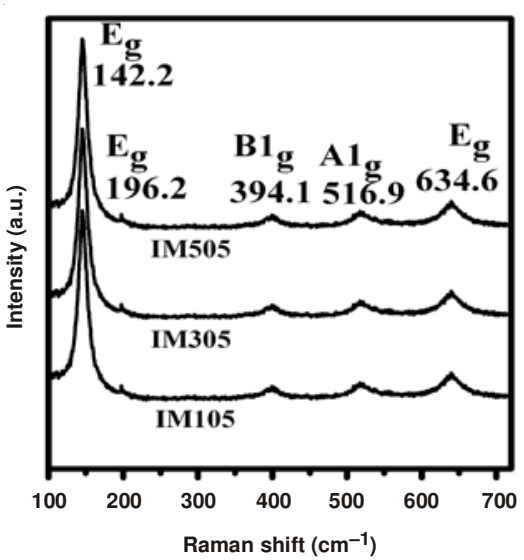

Fig. 2. Raman spectra for resultant films

Raman active modes centered around 142, 196, 394, 517 and 635 cm^{-1}, which are found to be matching with Raman spectrum for single crystal anatase TiO_2[15]. Due to nanocrystalline nature of films, 2 active modes at 512 (A_{1g}) and 519 (B_{1g}) cm^{-1} are not resolved all spectra[15]. These observations consistent with XRD results confirm formation of pure anatase TiO_2 in all films. Fig. 3 shows SEM photographs for resultant films (magnification = X10 K). All photographs show uniform size distribution of nearly soft spherical agglomerates containing many primary nano-sized particles.

The high resolution TEM photograph of IM505 film (Fig. 4a) shows spherical particles with average size = 20 nm. Fig.

TABLE-1
OPTICAL CHARACTERISTICS FOR RESULTANT FILMS

Film name	t (nm)	T% (675 nm)	$\alpha \times 10^4$ (cm^{-1})	E_g (eV)		n(λ = 675 nm)	$\sigma_{opt} \times 10^{12}\ s^{-1}$	P
				Indirect	Direct			
IM105	503	89.6	2.85	3.18	3.52	2.08	0.42	38.9
IM305	763	87.8	2.82	3.20	3.54	2.05	0.39	42.7
IM505	859	86.9	2.42	3.22	3.55	2.02	0.39	43.5

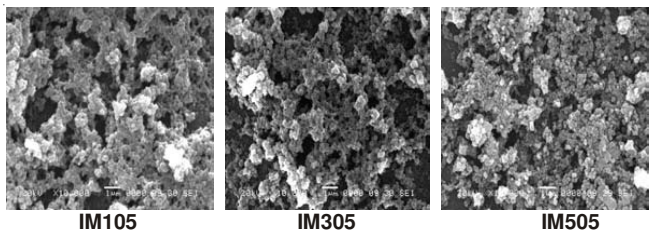

Fig. 3. SEM photographs for resultant films

4b) shows more number of crystalline grains having diameters between 15-20 nm in a structured matrix. The selected area electron diffraction (SAED) (inset-Fig. 4b) shows the ring pattern indicating thereby nanostructured nature of film. The interplaner spacing (Fig. 4c) obtained by using TIA software is found to be 0.23 nm, which is matching with reported value for $d_{(004)}$ plane of anatase TiO_2[14].

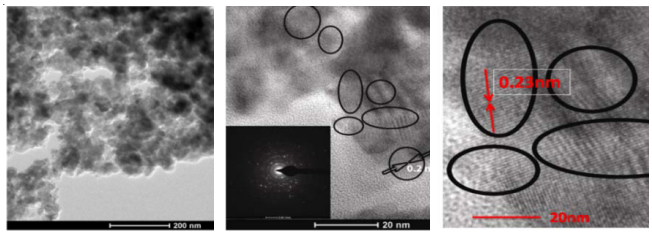

Fig. 4. TEM photograph (left), crystalline grains with SAED (middle) and micrograph TIA software processed image (right) of IM505 film

The optical properties obtained from UV-visible transmittance (T %) spectra for all films (Fig. 5a) are given in Table- 1. All films have average moderate T% = 86-90 with absorption edge around 300 nm. This is due slightly higher annealing temp. = 400 ºC leading more scattering of light. The values of absorption coefficient (α)[16]: $\alpha = -\frac{1}{t}\ln\left(\frac{1}{T}\right)$ are found to between 2.85-2.42 × 10^4 cm^{-1}. Fig. 5 (b) and (c) give the Tauc plots[17] for optical indirect and direct band gaps (E_g) of films respectively obtained by using the relation: $\alpha h\nu = A(h\nu - E_g)^r$, [$h\nu$ = photon energy, A = constant, r = 1/2 for indirect and r = 2 direct optical transitions] direct band gap of resultant films.

The extrapolation of linear region of plot to the energy axis gives the band gap energy. The values of optical conductivity σ_{opt} of films obtained by using the relation[18]: $\sigma_{opt} = \frac{\alpha nc}{4\pi}$ [where c = velocity of light] are found to be between 0.39-0.42 × 10^{12} s^{-1}. The optical properties: T % (at λ = 675 nm), α and σ_{opt} are found to be decreasing with increasing film thickness (d) as is expected. The refractive indices (n) of films obtained by using envelope method[19] (Table-1) are found to be slightly decreasing with increasing the d. This can be attributed to lower packing density[20] of film at higher d value.

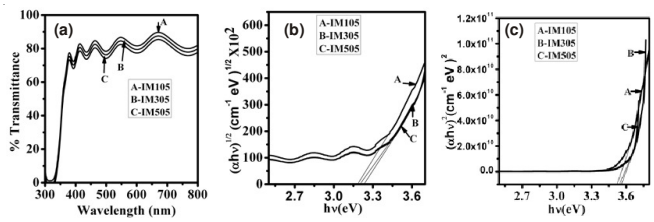

Fig. 5. (a) UV-visible % transmittance spectra, (b) indirect energy band gap and (c) direct band gap

The porosity (% P) of films obtained by using the relation[7]: P = 1-(n_p^2-1)/(n^2-1) [where, n_p and n = refractivity of porous and bulk films respectively] are found to be 38-44. The optical properties: indirect-direct E_g and % P are found to be slightly increasing with increasing the d (Table-1).

This might be due to the preparation conditions of films leading to the similar morphological nature and constant particle size distribution irrespective of coating layer number (Fig. 4). The Fig. 6(a) and (b) give the current density (J_{sc})-voltage (V) curves for dye sensitized solar cells of resultant films for Eosin-Y and Rose Bengal dyes respectively. The photovoltaic properties obtained are summarized in Table-2. The efficiency (η) of dye sensitized solar cell is found to be increasing with increasing the 'd' for both the dyes.

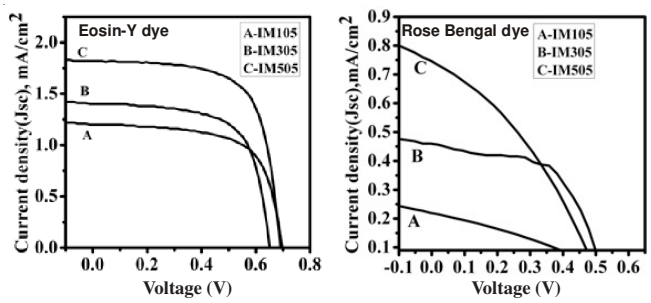

Fig. 6. J_{sc}-V characteristic curves for resultant films

The better photovoltaic properties: V_{OC} = 0.70 V, J_{SC} = 1.82 mA/cm^2, FF = 68.31 % and η = 0.87 % are obtained for IM505 film for Eosin-Y dye. This might be due to the optimum porosity required for absorption of Eosin-Y dye in film material. The efficiency is found to be enhanced due to nanocrystalline nature of films as compared to reported data (η = 0.16 to 0.60 %) for same dye and different materials[21,22].

Conclusion

The sol-gel dip-coating is easy method for preparation of nanocrystalline-pure anatase TiO_2 films. The optical properties: (i) T %, α, n and σ_{opt} and (ii) E_g and % P are found to be decreasing and increasing respectively with increasing the film thickness. The conversion efficiency of nanocrystalline-TiO_2 film based dye sensitized solar cell is found to be increasing

TABLE-2
PHOTOVOLTAIC CHARACTERISTICS FOR RESULTANT FILMS

Dye used parameter and film	Eosin-Y dye			Rose Bengal dye		
	IM105	IM305	IM505	IM105	IM305	IM505
Thickness d (nm)	503	763	859	503	763	859
Open circuit voltage, V_{oc}	0.694	0.696	0.700	0.512	0.406	0.407
Short circuit current, I_{sc} (μA)	307	348	455	115	225	809
Current density, J_{sc} (mA/cm2)	1.22	1.4	1.82	0.459	0.898	0.326
Fill Factor, FF (%)	65.79	67.21	68.31	58.13	42.13	33.47
Efficiency, η (%)	0.55	0.65	0.87	0.14	0.15	0.43

with increasing the film thickness for Eosin-Y and Rose Bengal dyes. The better photovoltaic properties: FF = 68.3 % and η = 0.87 % using Eosin-Y dye with polyiodide electrolyte are obtained for IM505 film.

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