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Studies on pure and Ce doped TiO_2 thin films prepared by sol-gel technique

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Abstract : Developments of high efficiency TiO_2 thin films based dye sensitized solar cells (DSSCs) have been interesting for last two decades. The pure and Ce doped TiO_2 thin films were deposited by sol-gel spin coating technique. The phase identification was carried out by X-ray diffraction analysis, it revealed that the prepared thin films were anatase phase. The crystallinity of the prepared thin films was investigated by micro Raman spectroscopy. Ce doped TiO_2 thin film showed good crystallinity compared with pure TiO_2 thin film. Surface texture changes were noticed by scanning electron microscopy analysis. The emission properties and atomic vacancies of the deposited thin films were studied by photoluminescence spectroscopy. Transmittance spectra of the pure and Ce doped TiO_2 thin films were recorded by UV-Vis spectrometer, the wavelength of the Ce doped thin film was in red shifted toward to higher value compared to pure TiO_2 thin films.
Keyword: DSSCs, TiO_2, micro Raman spectroscopy, sol-gel spin coating technique.

Introduction

Dye sensitized solar cells have been attracting significantly for over the couple of decades, it is a third generation solar cell. Titanium dioxide is an indirect band gap semiconductor and also has band gap energy 3.2 eV similar to zinc oxide. TiO_2 is one of the most interesting an n-type semiconductor material to construct the DSSCs[1]. Which is typically consist of TiO_2 nanocrystalline thin films as a photo anode, platinum as a counter electrode and iodine solution is used as an electrolyte. The highest photo conversion efficiencies of DSSCs have been obtained by using TiO_2 photo anode and ruthenium dyes. TiO_2 thin films have been prepared by several methods such as chemical vapor deposition, electrodeposition, pulse laser deposition, chemical spray pyrolysis, hydrothermal, sol-gel and glancing angle deposition [2]. Among them, sol-gel spin coating method is low cost, simplicity and easy to control the thickness of the films, hence in the present study.

Experiment

Pure and Ce doped TiO_2 thin films were prepared by sol-gel spin coating method[3]. The precursor solution containing a mixture of 0.05 M titanium tetraisopropoxide and different doping ratio of cerium nitrate hexahydrate (Ce= 0 and 1%) was dissolved in isopropanol. The solution was continuously stirred at room temperature for 30min. Then the mixture of ethanol and deionized water was added drop by drop in the solution

and stirred up to 30 min. The pH of the solution was adjusted by adding diluted HCl in the range of 3-4. Subsequently, the solution was stirred to hydrolysis reaction for 1h. Before the deposition, the substrates were cleaned with chromic acid, ethanol, deionized water and acetone. The thin films were deposited at 4000 rotations per minute (RPM) for 30 Sec. After the deposition, the films were pre-heated at 100˚C to remove the organic solvent present in the thin films. The deposition process was repeated for three times to increase the film thickness. Finally, all the films were annealed at 500˚C for 3 h.

Results and Discussion

Structural analysis

Structural analysis of pure and Ce doped TiO_2 thin films prepared in sol-gel technique annealed at 500˚C for an hour were carried out by X-ray diffraction and is shown in fig.1. The diffraction peaks at 25.18˚ and 48.2˚ are corresponding to (101) and (200) plane, which is consistent with JCPDS card no 89-4921 for TiO_2 anatase phase. There is no other impurity peaks appeared in pure and 1% of Ce doped prepared thin film, it explore that the dopant have incorporated well with TiO_2 material. The crystalline sizes of the pure and doped TiO_2 thin films are calculated by using Scherrer formula[4].

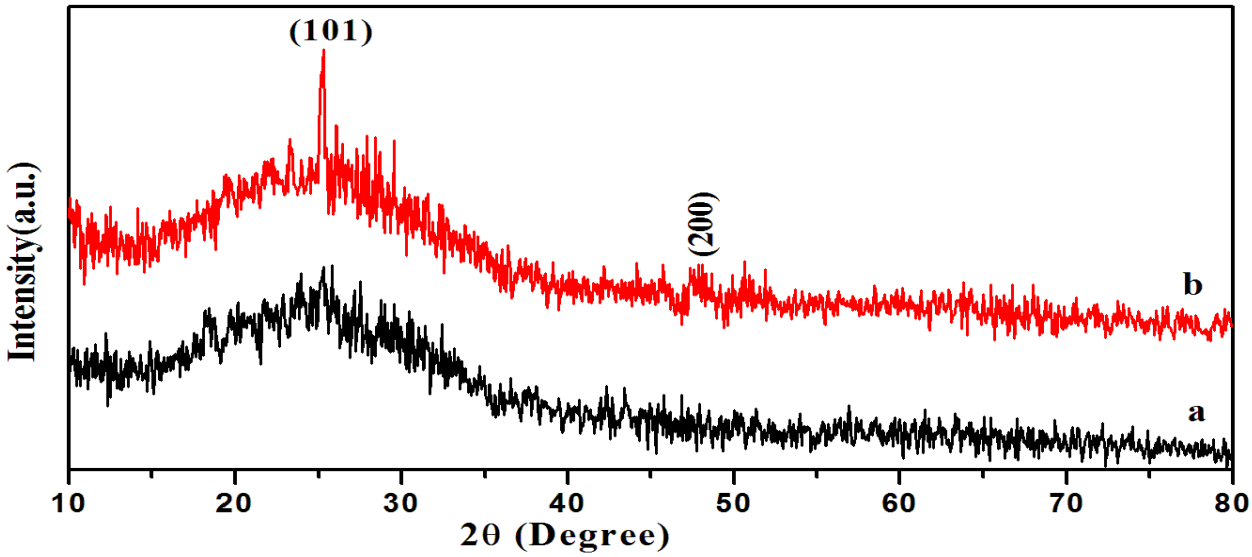

Figure 1. XRD pattern of the pure and doped thin film: (a) 0% and (b) 1% of Ce.

Table 1. Crystalline size, dislocation density and Micro strain.

Sample code	Doping concentration of Ce (%)	Crystalline Size (nm)	Dislocation Density 10^{14} (lines/m^2)	Micro Strain 10^{-3} (lines^{-2}m^{-4})
a	0	8	150.8	3.8
b	1	32	9.42	0.95

Morphological Analysis

Morphology of the pure and Ce doped TiO2 thin films prepared by sol-gel method annealed at 500˚C were observed by scanning electron microscope. The fig. 2 shows an SEM micrograph of the pure and doped TiO_2 thin film prepared at 4000RPM. The particles are agglomerated and uniformly distributed over the surface of the substrate for pure TiO_2 thin films as shown in figure (2a). When 1% of Ce is doped with TiO_2 thin film, the particles are not uniformly agglomerated and the agglomerated particles have been shown as a rock like structure, which has revealed well crystalline from XRD analysis. The composition analysis has been carried out for Ce doped TiO_2 thin films and the presents of Ti, Ce and O are confirmed from EDAX s.

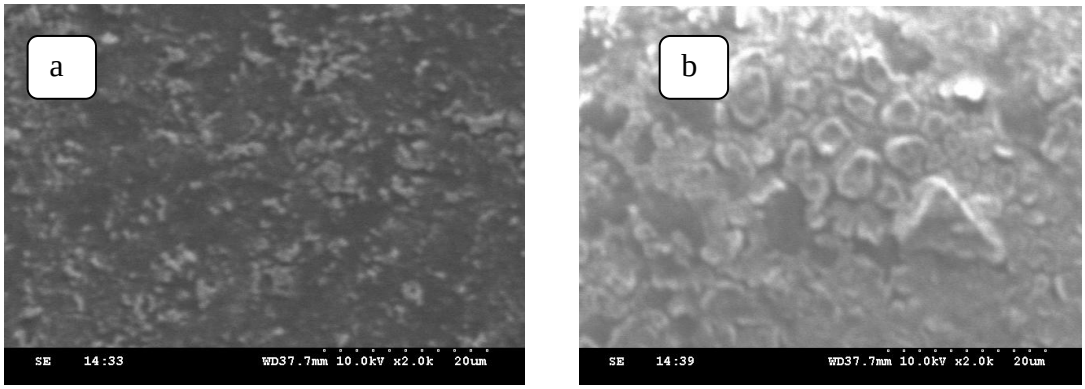

Figure 2. SEM micrograph of TiO_2 thin film (a) pure and (b) 1% Ce dopant.

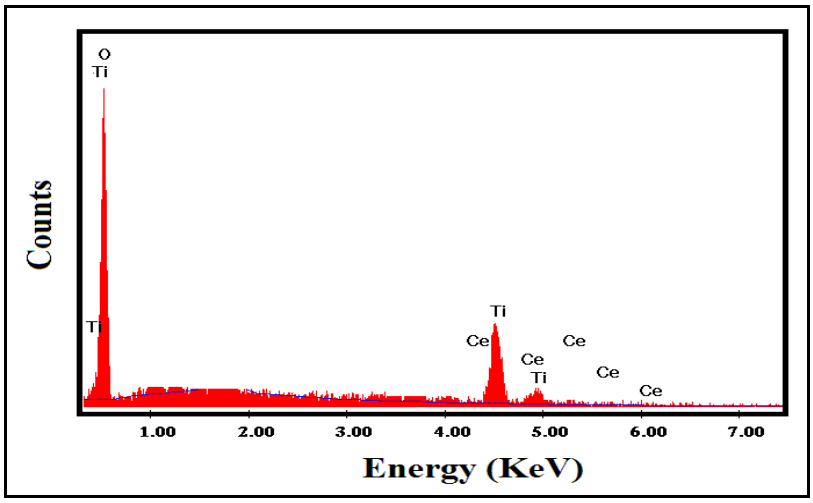

Figure 3. EDAX spectrum for Ce doped TiO_2 thin film.

Table 2. Elemental compositions for Ce doped TiO_2 thin film in atomic percentage.

Sample code	Ti	O	Ce	Total (atomic percent)
b	11.19	87.86	0.95	100

Raman spectroscopy

Raman scattering has been carried out from micro Raman spectrometer, the obtained spectra are shown in fig. 4. It is one of the most effective tools to study of crystallinity, defect structure associated with the materials[5]. According to group theory, anatase phase has six Raman-active modes (A1g +2B1g +3Eg)[6]. There are four peaks appeared at 153 (E_g), 395 (B_{1g}), 514 (A_{1g}) and 634 cm^{-1} (E_g) in pure and Ce doped TiO_2 thin films. From the Raman spectra, it is evident that both the pure and Ce doped TiO_2 thin films are in an anatase phase. There is no impurity-related mode appeared in the Raman spectra of the dopant sample. When 1% of Ce is doped in TiO_2 thin film, the intensity of the Eg peak is decreased and broadened. This is due to the reduction of particle size in the Ce doped sample. The crystalline size in the nanoscale range has affected broadening of Raman peaks due to the photon confinement[7]. The reduction of scattering intensity particularly in the Eg peak is ascribed due to the breakdown of long range translational crystal symmetry caused by the incorporated defects[8].

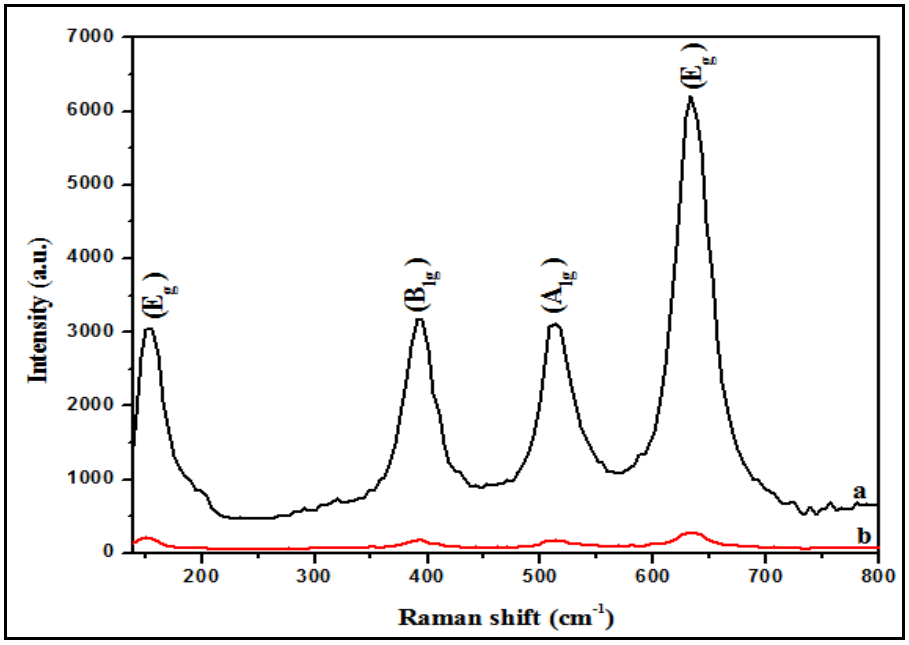

Figure 4. Micro Raman spectra of the TiO_2 thin film (a) pure and (b) 1% Ce.

PL spectra

Photoluminescence spectrum is primarily used to determine the effectiveness of trapping, migration and transfer of charge carriers in semiconductors[9]. Fig. 5 shows the PL spectra of the pure and doped samples recorded at room temperature in excitation 340 nm. The three peaks at 412,436 and 462 nm are appeared due to deep level emission in the visible region. The violet emission peaks at 412 and 436nm are originated from the self-trapped excitons localized on TiO_6 octahedral[10]. The blue emission peaks at 462 nm is attributed to oxygen vacancies[11]. It is interesting to note that for the 1% of Ce doped sample, the intensity of the violet and blue emission has decreased. It indicates that the relative intensity blue emissions have been tailored by adjusting the concentration of dopant ions in the TiO_2 lattice. However, the Ce doped TiO_2 thin film has exhibited low PL intensities compared to the pure TiO_2 thin film. This is attributed to the reduction of either oxygen vacancies and/or defects in Ce doped TiO_2 thin film, which leads to decrease in their optical properties. Therefore, the PL signal decreased with the decreasing content of oxygen vacancies or defects.

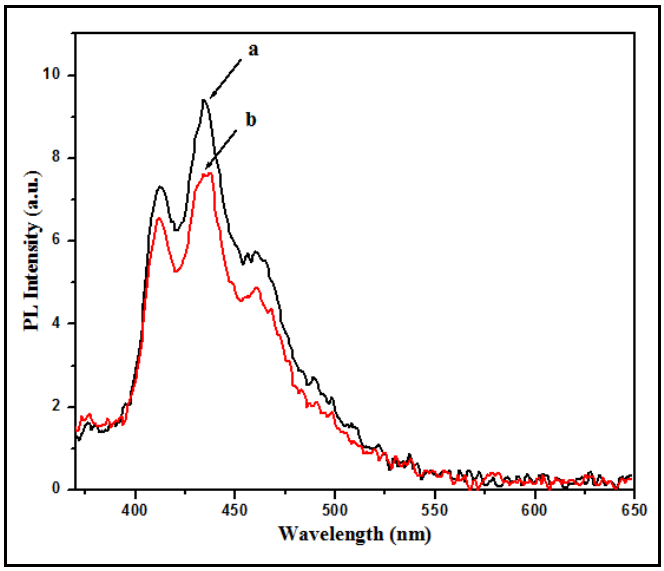

Figure 5. PL spectra of the TiO_2 thin film (a) pure and (b) 1% Ce doped.

UV Spectra

The transmittance spectra of the prepared pure and doped thin film have been recorded by UV-Vis spectrometer and are shown in fig. 6. From the spectra, one can observe that the films are transparent in the visible region and have showed absorption in UV region. When 1% of Ce is doped into TiO_2, the reduction of the transmittance is occurred and absorption band edge is red shifted toward to higher wavelength compared to pure TiO_2 thin film. It may be reduction of particle size, which is confirmed by Raman spectra. However, crystalline size from XRD has shown big compared to pure TiO_2 thin film.

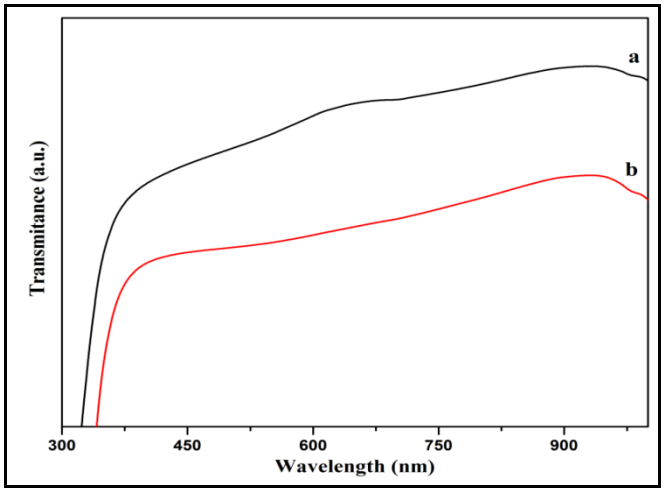

Figure 6. UV-Vis spectra of the TiO_2 thin film (a) pure and (b) 1% Ce doped.

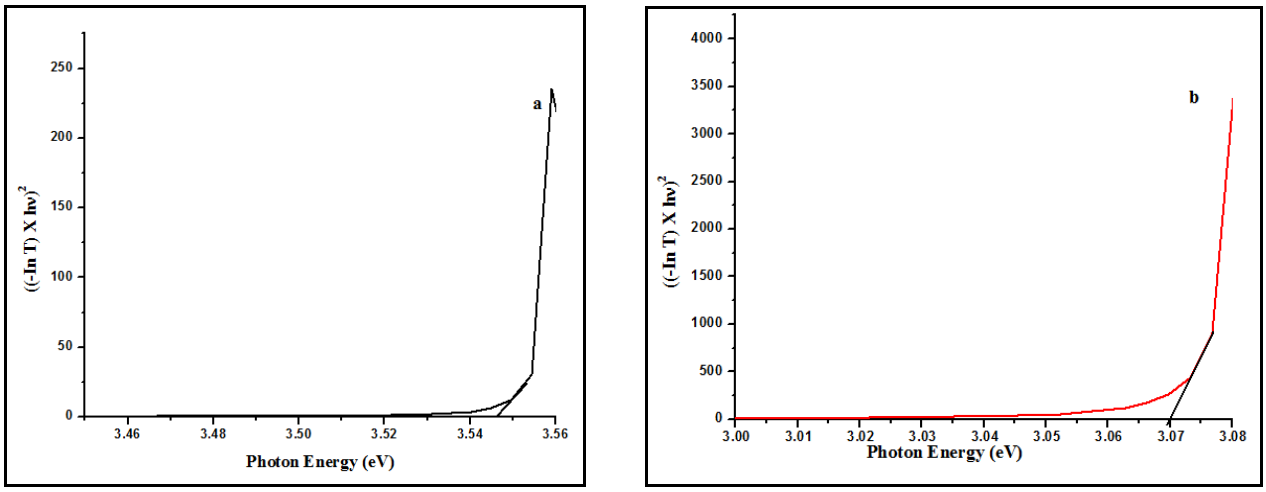

Figure 7. Band gap of the TiO_2 thin film (a) pure and (b) 1% Ce doped.

The band gap of the prepared pure and doped thin films has been calculated from the UV-VIS data by using the conventional Tauc equation[12].

$$\alpha h\nu = A(h\nu - Eg)^{n/2}$$

Where n=1 is for direct band gap, n=4 is for indirect band gap, A is a constant. The band gaps of the pure and doped thin film are calculated from the zero crossing value obtained by extrapolation of the $(\alpha h\nu)^2$ versus hν plot in figure (7), where hν is energy of the photon and α= (-lnT) is the absorbance coefficient[13]. Band gap of the pure and Ce doped TiO_2 thin films are 3.54eV and 3.07 eV respectively.

Conclusion

In this present work, pure and Ce doped TiO_2 thin films have been deposited by using sol-gel spin coating method. The structural, morphologies, crystallinity, photoluminescence and transmittance spectra have investigated. Anatase phase of the prepared pure and doped TiO_2 thin films has confirmed by XRD analysis.

The morphologies of the films have observed by scanning electron microscope. Crystallinity of the thin films has studied from Micro Raman spectroscopy. Luminescence properties of the prepared thin film have investigated by photoluminescence spectra. The transmittance spectra and band gap of the pure and doped thin films has obtained from UV-Vis spectroscopy.

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