

Structural investigations on nanocrystalline TiO₂ thin films prepared by sol-gel spin coating technique

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Nanocrystalline TiO₂ thin films have been prepared using titanium isopropoxide precursor by sol-gel spin coating technique. The prepared TiO₂ films have been annealed at different temperatures. The structural properties of the films have been studied by using x-ray diffraction method, high resolution transmission electron microscope(HRTEM) and Raman spectra. The as deposited films have been found to be amorphous in nature. The crystalline quality has been observed to improve with annealing temperature. The annealed TiO₂ films have been found to exhibit anatase phase. The grain size of the annealed TiO₂ films is found to be nearly 25 nm. The photoluminescence spectra of the films annealed at 550°C exhibit a strong band centered around 400 nm.

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1. Introduction

Many nanostructured materials are now being investigated for their potential application in photovoltaic, electro-optical, micromechanical and sensor devices [1]. Nanoporous TiO₂ thin films for dye sensitized and ETA solar cells have been under intensive study for many years [2]. TiO₂ occurs naturally as minerals: rutile, anatase or brookite. The anatase form have been intensively studied and have significant technological usefulness, owing in large measure, to their optical properties: transparent in the visible and absorb in the near ultraviolet [3]. Recent interest has been in the transparent anatase doped films [4]. TiO₂ thin films have been synthesized by various researchers using a wide variety of techniques such as chemical vapor deposition[5], aerosol pyrolysis [6], electrodeposition [7] and sol-gel method [8-15]. The sol-gel method allows simple production of high purity films at low cost and at low temperature without degrading the organic functional groups or the polymer. This paper reports on the structural properties and photoluminescence properties of the TiO₂ anatase films prepared by sol-gel derived spin coating method.

2. Experiment

The TiO₂ thin films have been prepared by the sol-gel spin coating process. Titanium isopropoxide TIP (Alfa Aaser 99.9%) has been used as the titania precursor, absolute ethanol (Aldrich 99.9 %) has been used as solvent and acetic acid as a catalyst, controlling the pH of the solution [16]. The matrix sol was prepared by mixing TIP with absolute ethanol and acetic acid (1:9:0.1) at room

temperature. Optically transparent clean glass slides have been used as substrates. The sol were deposited drop wise on the substrate, which was rotated at a speed of 3000 rpm for 35 seconds. Similar deposition process has been reported by Que and Uddin [16]. Then the as-coated films have been heated for 1 hour in air at different temperatures. The structural properties of the spin coated TiO₂ films have been studied using x-ray diffractometer(PANalytical) and high resolution transmission electron microscope(HRTEM) (Philips, TECNAI F20), AFM analysis were performed on the samples measuring the topography with a Digital instruments Dimension 3100 Scanning Probe Microscope operated in tapping mode and Raman spectroscopy using Jobin Yuon Lab Ram Spectrometer employing a single mode Ar-ion laser for excitation($\lambda = 488\text{nm}$) at a power of $\sim 4.4\text{mW}$. The photoluminescence studies have been carried out using Shimadzu-1501 spectrofluorometer using an excitation wavelength of 330 nm.

3. Results and discussion

The as deposited TiO₂ films are found to be amorphous in nature. The x-ray diffraction pattern of TiO₂ films annealed at 350, 450 and 550° C are shown in figure 1. The 350° C annealed film is also amorphous but the 450 and 550° C annealed films exhibit small peaks indicating the formation of nanocrystalline TiO₂ films. The peaks are not sharp indicating that the average crystallite size is small. Due to size effect the peaks in the diffraction pattern broaden and their widths become large as the

particles become smaller. Crystallinity is found to improve with increase in annealing temperature. The peaks have been indexed and found to be that of anatase TiO_2 .

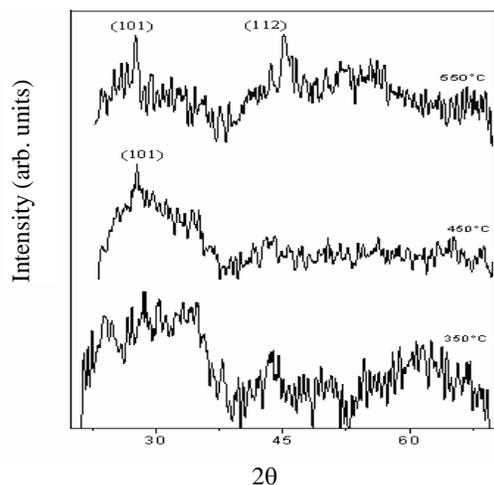


Fig. 1. x-ray diffraction pattern of annealed TiO_2 films

The peak corresponding to (101) plane is the characteristic peak of anatase phase. The average crystallite size has been estimated from the integral width of the diffraction peaks using Scherrer formula and is 20 nm and 25 nm for the 450 and 550 °C annealed samples. No peak corresponding to the rutile phase of TiO_2 has been detected. The lattice parameter values a and c corresponding to the tetragonal anatase phase have been calculated and are 3.51 and 9.62 Å respectively.

The high resolution transmission electron microscope (HRTEM) image of the spin coated TiO_2 film annealed at 550° C is shown in figure 2. The figure shows that the structure of the prepared films is anatase cubic having an average particle size of 25 nm. The HRTEM image exhibits lattice fringe patterns with d spacing of 0.389 nm corresponding to the interplanar distance $d_{101} = 0.389$ nm of the

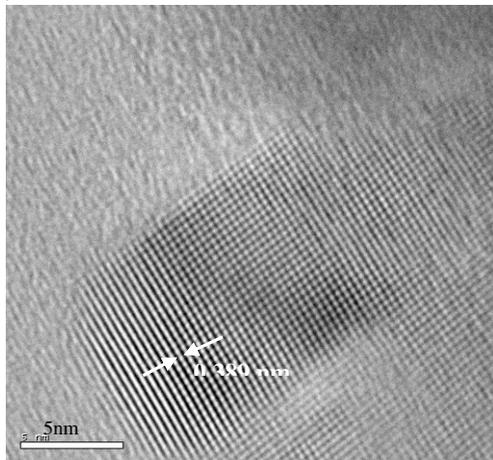


Fig. 2. HRTEM image of 550 °C annealed TiO_2 film.

anatase TiO_2 phase. The composition of the prepared TiO_2 films have been analyzed using energy dispersive x-ray analysis and is titanium – 33.33 at% and oxygen 66.67 at%. Figure 3 shows the atomic force microscope image of the spin coated TiO_2 film annealed at 550 °C. The image shows well defined particle like features with granular morphology and indicates the presence of small crystalline grains. Because of the heat treatment the crystalline phase has formed and this leads to the

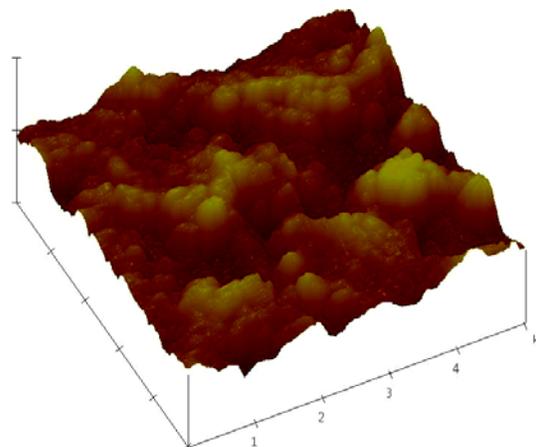


Fig. 3. Atomic force microscope image of 550 °C annealed TiO_2 film.

appearance of grains making the films to have higher surface roughness. The root mean square surface roughness of the films is 92 nm.

The Raman spectra of TiO_2 film annealed at 550° C is shown in figure 4. The Raman spectra is distinct without overlapping of peaks suggesting that the prepared films are well crystallized with low level of impurity sites. The vibration peaks present in the spectra at $145 \text{ cm}^{-1}(\text{E}_g)$, 394 cm^{-1}

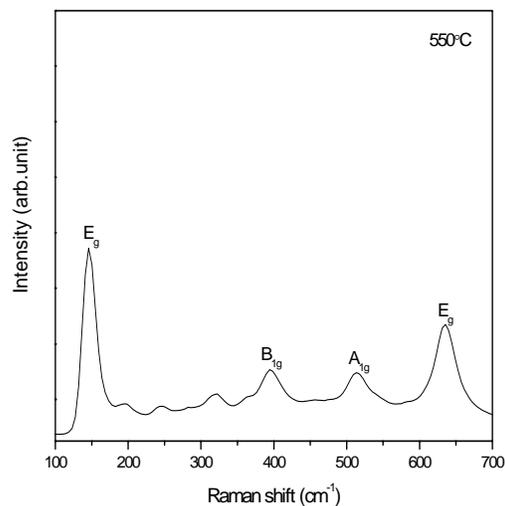


Fig. 4. Raman spectra of 550 °C annealed TiO_2 film.

(B_{1g}), 513 cm⁻¹(A_{1g}) and 635 cm⁻¹(E_g) unambiguously correspond to the Raman active modes of the anatase phase of TiO₂. Anatase has six Raman active modes: A_{1g}+2B_{1g}+3E_g. The presence of rutile phase was not detected in the Raman spectra also, confirming the x-ray diffraction and HRTEM results. The photoluminescence spectra of the 550 °C annealed TiO₂ film is shown in figure 5. The spectra exhibits a visible broad band in the region of 350 to 550 nm. The intensity of PL signal is found to be strong. The PL of anatase TiO₂ can be interpreted as due to the recombination via self trapped excitons located or trapped on TiO₆ octahedra and this originates from the defect states present. The oxygen impurities are a kind of intrinsic defects in TiO₂ lattice and form intermediate energy levels within TiO₂ band gap introducing many recombination centres of photoinduced electrons and holes.

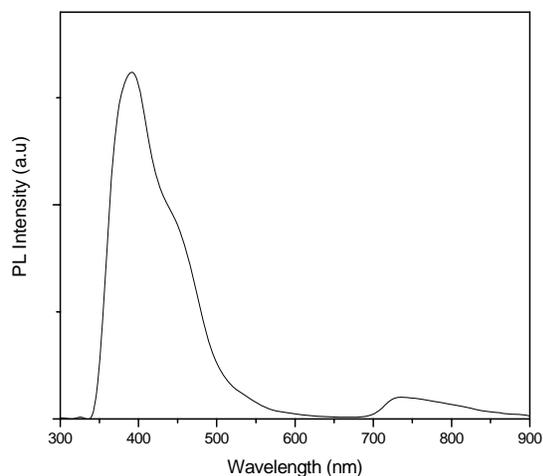


Fig. 5. Photoluminescence spectra of 550 °C annealed TiO₂ film.

4. Conclusion

TiO₂ thin films have been prepared by the sol-gel spin coating technique. The structural studies carried out on the deposited films indicated that the films are nanocrystalline in nature with grain size around 25 nm exhibiting the anatase phase. TiO₂ thin films with anatase phase has been reported to be most suitable for solar cell applications. The photoluminescence studies have indicated the presence of defect levels leading to luminescence.

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