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Growth and characterization of optically confined particulate films of anatase TiO_2

Prakash Thanigainathan[1*] and Chandrasekar Paramasivan[2]

Abstract

TiO_2 particulate films with optically confined anatase phase were deposited on glass substrates using an aqueous precursor by dip-coating method. The precursor solution was prepared by mixing appropriate amounts of titanium tetraisopropoxide, isopropyl alcohol, and Triton X-100 in an airtight vessel. Without further treatment, the solution was used for the coating process. After deposition, the films were baked at 300°C, 450°C, and 600°C for 15 min in air atmosphere using a box furnace. Physical properties of such films were investigated by X-ray diffraction, scanning electron microscopy, and UV-visible spectrophotometry. Effective mass approximation theory was applied to explain the optical confinement effect which is realized in those films because of its crystallite size. The energy bandgap values for the confined anatase phase of TiO_2 particulates were predicted by the effective mass approximation model and are in good agreement with our experimental results. These observed results were discussed in detail.

Keywords: Transparent semiconductor, Optical properties, Effective mass approximation theory

Background

Nanotechnology is a frontier field of research with far-reaching implications for novel applications. Its projected potential in this respect has led to a significant growth of activity in the synthesis of nanomaterials in different shapes and sizes with stoichiometric perfection. Nanocrystalline TiO_2 films are attracting considerable attention because of their technological applications that include dye-sensitized solar cells [1], varistors [2], sensors [3], photocatalysts [4], and electrochromic windows [5]. In all these applications, films with a combination of properties such as optical transparency and chemical stability with high surface area are strongly required. In fact, TiO_2-coated tiles with self-cleaning and bactericidal functions have been already commercialized [6]. When compared with the other two phases, brookite (orthorhombic) and rutile (tetragonal), the anatase (tetragonal) phase has been a subject of research during the last few decades because of its properties and increasing demand for its applications. Several techniques such as chemical vapor deposition [7], pulsed laser deposition [8], ion-assisted electron beam evaporation [9], and atomic layer deposition [10] are commonly used to prepare the anatase TiO_2 films. All these techniques require vacuum chambers and costly precursor materials. Hence, there is a need for developing or optimizing preparation conditions for viable low-cost solution-based processes which yield high surface area films. In the present work, homogeneously nucleated particles were utilized for the growth of anatase TiO_2 films having high surface area on glass substrates. The films were deposited and crystallized after baking at different temperatures for different periods and then studied for its characteristics; the observed results are discussed with suitable theory.

Methods

To the typical growth of TiO_2 films on glass substrate, 5 mL titanium isopropoxide (97%, Sigma-Aldrich Corporation, St. Louis, MO, USA) was added into the solution that consists of 75 mL isopropyl alcohol and three drops of Triton X-100 and then rapidly stirred for 60 min in an airtight vessel. Without any further treatment, the solution was used for dip-coating process using one side-masked well-cleaned glass substrates. It led to the rapid growth of particulate coatings. These films are slightly brownish yellow in color after baking

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at 300°C for 15 min, but white color was observed for films which are baked at 450°C or 600°C for 15 min in air atmosphere using a box furnace. Structural properties of all those films were investigated using X-ray diffractometer (XRD) (X'Pert high scorer, PANalytical BV, Almelo, The Netherlands) equipped with CuKα_1 radiation (λ = 1.5406 Å) and a step size of 0.02°/sec. The surface morphology of the thin films was studied by scanning electron microscopy (SEM) (JSM 840-A, JEOL Ltd., Akishima, Tokyo, Japan). Optical qualities of all the three samples were investigated using a UV-1800 Shimadzu (Shimadzu Corporation, Na kagyo-ku, Kyoto, Japan) UV-visible (vis) spectrophotometer between the wavelength range of 200 to 900 nm. Commercial scientific software Origin 6.1 (OriginLab Corporation, Northampton, MA, USA) was used to plot the spectra and in some cases even for analysis of the spectra.

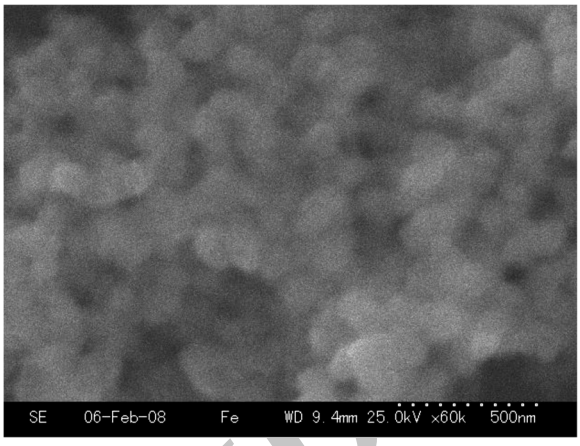

Figure 2 SEM image of particulate TiO_2 film baked at 600°C for 15 min.

Results and discussion

XRD patterns of TiO_2 films baked at 300°C, 450°C, and 600°C for 15 min is shown in Figure 1. All the patterns were fully indexed with JCPDS XRD file 89–4921 using XRDA 3.1 software [11]. The analysis confirms the existence of crystallites in tetragonal crystal structure without any impurity phase within the detection limits of the XRD instrument in the scanned region 20° to 70°. SEM image of the film baked at 600°C is shown in Figure 2. The image analysis reveals that the crystallites present in the films are spherical in morphology and are well adhered on the glass substrate. UV–vis absorbance spectra of all three anatase TiO_2 films are shown in Figure 3. The absorbance onset value for all the three samples was estimated by extrapolating the absorbance edge, and it was found to be 360.6, 364.6, and 372.2 nm for films baked at 300°C, 450°C, and 600°C for 15 min, respectively. In general, the shape of the absorption spectrum in the vicinity of the absorption edge for a bulk semiconductor is usually determined by the nature of electronic transition from the valence band to the conduction band. If the dimension of the nanocrystalline semiconductor particles becomes smaller than the exciton Bohr radius, quantum confinement leads to the size-dependent enlargement of the bandgap and results in a blueshift in the absorbance onset. In the present case, the absorption onset of all three samples made a blueshift relative to the bulk form of anatase phase of TiO_2, which is known to occur at 390 nm. Widening of trapping levels in the energy bands is fundamental for the observed blueshift in the absorption onset, which indicates that the nanoparticles formed are in the quantum dot regime.

Widening of the bandgap is expected in nanocrystalline semiconducting materials because relatively flat

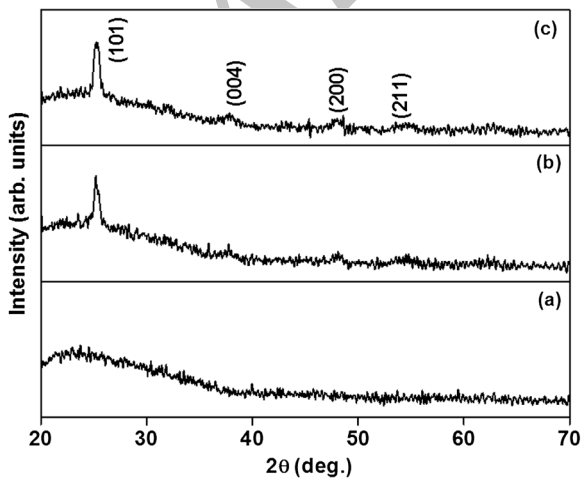

Figure 1 XRD patterns of particulate TiO_2 films. They were baked at (**a**) 300°C, (**b**) 450°C, and (**c**) 600°C for 15 min.

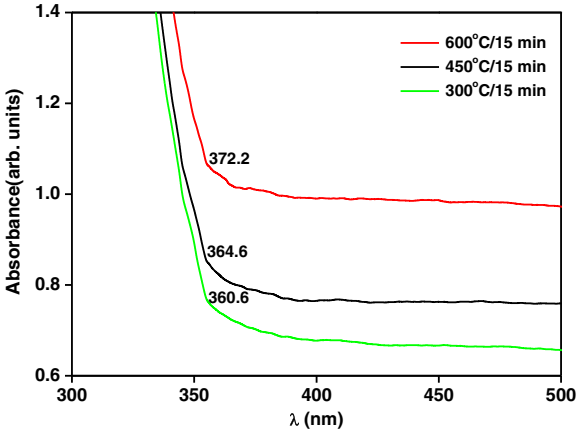

Figure 3 UV–vis absorbance spectra of particulate TiO_2 films baked at different temperatures.

bands possessing both properties of delocalized long-range-ordered bands and localized states originating from confinement effects begin to play a principal role and possess relatively high electron–phonon interactions [12]. Kityk recently reported [13] the significant electron-photon anharmonic contributions in nonlinear optical properties of nanocrystallites. The relationship between the bandgap and crystallite size can be obtained using a number of models. In the present work, such a calculation for TiO_2 sample was carried out using the following equation proposed by Brus [14] for the lowest direct inter-band transition energy of confined spherical nanoparticles of radius R in the effective mass approximation:

$$E_g^* \approx E_g + \frac{\pi^2 \hbar^2}{2R^2}\left[\frac{1}{m_e}+\frac{1}{m_h}\right] - \left[\frac{1.8e^2}{\varepsilon R}\right] \quad (1)$$

where E_g and E_g^* are bandgap values of the bulk and confined crystallites, respectively; ε is the dielectric constant, R is the radius of the crystallite, e is the charge of electron, m_e is the effective mass of electron, and m_h is the effective mass of hole. The second and third terms in the right-hand side correspond to the quantum localization energy and Coulomb potential, respectively. Absorption onset for all input values of radius was calculated since the bandgap is inversely proportional to the wavelength using the Equation 1, and the observed plot was shown in Figure 4. Corresponding bandgap enlargement ($\Delta E_g = E_g^* - E_g$) for different crystallite sizes was shown in Figure 5. Since the effective masses for electrons (0.8) and holes (10) in TiO_2 are relatively small [15], the bandgap enlargements can be seen for crystallite diameters of approximately <15 nm. The bandgap could be calculated using the absorption onset obtained from the absorption spectra using the relations $E_g = 1{,}239.8/\lambda$ (in nanometers). The obtained bandgap values for the samples baked at 300°C, 450°C, and 600°C are 3.44, 3.40, and 3.33eV TiO_2, respectively. These bandgap values clearly reveal that our coating process yields well-adhered optically confined particulate films since the bulk bandgap of anatase is 3.2 eV. Also, from Equation 1, the average crystallite diameter for the sample baked at 450°C and 600°C for 15 min was found to be 3 and 4 nm, respectively.

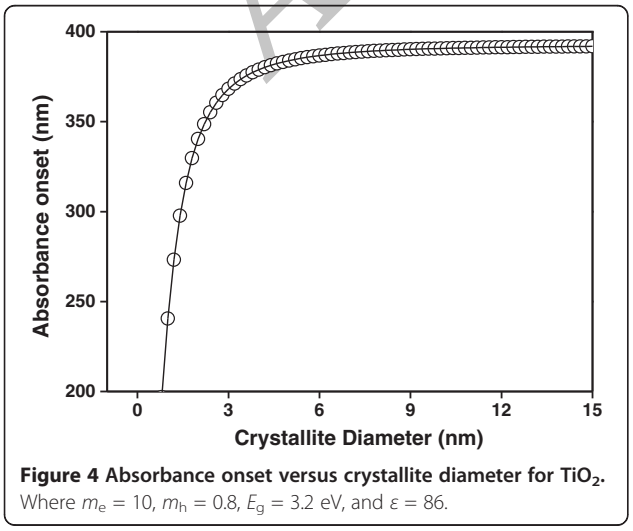

Figure 4 Absorbance onset versus crystallite diameter for TiO_2. Where $m_e = 10$, $m_h = 0.8$, $E_g = 3.2$ eV, and $\varepsilon = 86$.

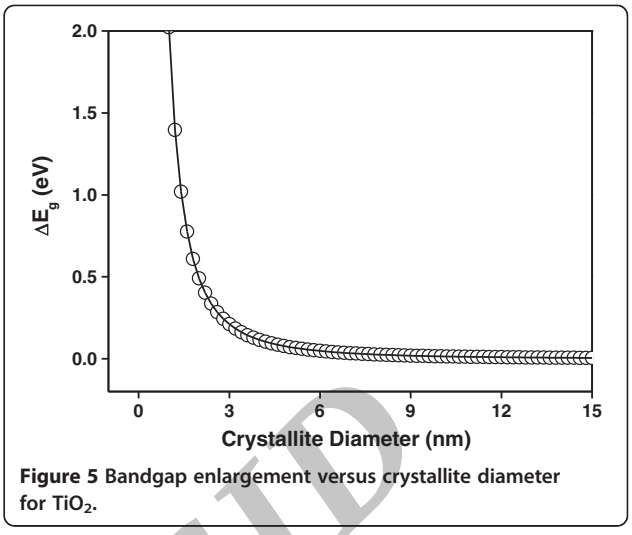

Figure 5 Bandgap enlargement versus crystallite diameter for TiO_2.

Conclusions

Rapid growth of anatase TiO_2 particulate films using a solution precursor by dip-coating process was demonstrated, and its physical properties were investigated using XRD, SEM, and UV–vis spectrophotometer. Effective mass approximation theory was applied to explain the optical confinement effect which is realized in the films because of its crystallite size. Also, the energy bandgap values for the confined TiO_2 particulates predicted by the effective mass approximation model are in good agreement with our experimental results. Since our growth process yields low-cost as well as optically confined films, it can be applied to fabricate optoelectronic devices such as dye-sensitized solar cells which need films with high surface area.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

Both authors, PT and CP, contributed equally to this manuscript. Both authors read and approved the final manuscript.

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