Investigation of optical, structural and morphological properties of nanostructured boron doped TiO₂ thin films

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Abstract. Pure and different ratios (1, 3, 5, 7 and 10%) of boron doped TiO₂ thin films were grown on the glass substrate by using sol-gel dip coating method having some benefits such as basic and easy applicability compared to other thin film production methods. To investigate the effect of boron doped on the physical properties of TiO₂, structural, morphological and optical properties of growth thin films were examined. 1% boron-doping has no effect on optical properties of TiO₂ thin film; however, optical properties vary with > 1%. From X-ray diffraction spectra, it is seen that TiO₂ thin films together with doping of boron were formed along with TiB₂ hexagonal structure having (111) orientation, B₂O₃ cubic structure having (310) orientation, TiB_{0.024}O₂ tetragonal structure having rutile phase (110) orientation and polycrystalline structures. From SEM images, it is seen that particles together with doping of boron have homogeneously distributed and held onto surface.

Keywords. Boron doped TiO₂; nanoparticles; thin films; optical and morphological characterizations.

1. Introduction

Titanium dioxide (TiO₂) is drawing the attention of researchers worldwide, especially due to its unique properties such as high transparency in the visible range with a wide bandgap, absence of toxicity, abundance in nature and good chemical stability in adverse environment, etc. The structural and optical properties of TiO₂ have made it a fascinating material for applications in solar cells (Minutillo *et al* 2008; Zhang *et al* 2012), photocatalysis (Tavares *et al* 2007), for adsorption of proteins (Topoglidis *et al* 2000), single or multilayer optical coatings (Ray *et al* 2007), dye-sensitized solar cells (O'Regan and Grätzel 1991). These physical properties depend on its atomic distribution and can be changed by doping TiO₂ with different dopants.

It is well known that with doping by different types of non-metallic ions like N (Sakthivel *et al* 2004; Reyes-Garcia *et al* 2007), C (Park *et al* 2006), F (Li *et al* 2005) and P (Yu *et al* 2003), physical properties of TiO₂ could be modified for optoelectronic applications. Compared with these non-metal dopants, boron (B) has been much less studied (Grey *et al* 1996; Zhao *et al* 2004). It is also known that B element has a similar ionic radius to Ti, therefore, it is possible that B enters into TiO₂ lattice.

Furthermore, to improve chemical and physical properties of TiO₂ thin films, researchers are trying to modify the synthesis procedure. Additionally, recently, there has been a

dramatic progress on the development of cost-effective thin film deposition techniques, especially in the field of optoelectronic technology in order to economize the technology. Different physical and chemical deposition techniques such as spray pyrolysis (Oja *et al* 2004), sol-gel (Pleneta *et al* 2000), sputtering (Singh *et al* 2009), pulsed-laser deposition (Giacomo and De Pascale 2004), plasma oxidation (Tinco *et al* 2003), chemical bath deposition (Morea *et al* 2008), etc have been employed to prepare TiO₂ thin films. Among these techniques, sol-gel is simple, inexpensive, non-vacuum and low temperature technique for synthesizing films. This process offers many benefits like perfect control of the stoichiometry of precursor solutions, ease of compositional modifications, customizable microstructure, ease of introducing various functional groups, requiring relatively low annealing temperatures and possibility of coating over large area substrates (Senthil *et al* 2010; Sönmezoğlu *et al* 2011, 2012).

Aim of the present study is to prepare the nanostructured pure and different ratios (1, 3, 5, 7 and 10%) of boron doped TiO₂ thin films on the glass substrate by using sol-gel dip coating method. The structural, morphological and optical properties of growth thin films were examined in detail to investigate the effect of boron doping on the physical properties of TiO₂.

2. Experimental

In order to prepare pure TiO₂ solution, first, 2-4 mL titanium tetraisopropoxide [Ti(OC₃H₇)₄, ex. Ti ≥ 98%, Merck], 5 mL

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glacial acetic acid [$\text{C}_2\text{H}_4\text{O}_2$, 99.9%, Merck] and 1.5 mL triethylamine [$(\text{C}_2\text{H}_5)_3\text{N}$, 99%, Merck] were added in 100 mL ethanol [$\text{C}_2\text{H}_6\text{O}$, 99.9%, Merck] and the solution was kept in a magnetic stirrer for 2 h. The solution was aged at room temperature for 1 day. Microscope glass slides were used as the substrates for thin films. Prior to deposition, the glass slides were sequentially cleaned in an ultrasonic bath with acetone and ethanol.

Triisopropyl borate ($\text{C}_9\text{H}_{21}\text{BO}_3$) was used as a boron source. To prepare the various rates (1, 3, 5, 7 and 10%), B-doped TiO_2 and pure TiO_2 solutions were prepared as mentioned above and then for 1; 3; 5; 7 and 10% ratios, 0.4, 1.2, 2, 2.8 and 4 mL $\text{C}_9\text{H}_{21}\text{BO}_3$ was added into the solution, respectively and mixed for 2 h. The final solution was aged at room temperature for 1 day before deposition.

After the above treatment, dip coating process was applied to cover TiO_2 solution on the glass substrates. The dipping process was performed using computer-controlled Holmarc–Dip Coating Unit and each sample was dipped into solution ten times. After each dipping process, samples were subjected to repeated annealing processes at a temperature of 500 °C for 5 min and finally post-annealed at a temperature of 500 °C for 1 h.

3. Results and discussion

In order to analyse the effect of B doping on the optical parameters of TiO_2 thin films, the optical transmission spectra was investigated for TiO_2 thin films in the wavelength range 300–1100 nm. Figure 1 shows UV–Vis spectra of TiO_2 thin films for various dopant concentrations. It is clear from figure 1 that pure and 1% B-doped TiO_2 thin films have the

Figure 1. Transmittance spectra of pure and B-doped TiO_2 thin films.

highest transparency with the same value of 93.72%. However, when B concentration in the solution is increased, the shift in the transmission spectra decreased, probably due to disorder in the lattice with the increase in localized states near to the bands. The values of maximum transmittance in the visible region are shown in table 1.

In general, the well oscillating transmittance curve can be observed in thin films, indicating its low surface roughness and good homogeneity. Besides, high transparency indicates a uniform thickness and a smooth surface as well as the film is specular to great extent. This presents quite useful interference maxima and minima because, from their spectral positions, the refractive index and thickness of the film can be easily calculated (Pankove 1971).

First approximate value of the refractive index of the films in the spectral region of medium and weak absorption can be calculated from the following relations:

$$n_{f(1,2)} = \left[\left(\frac{n_s(2 - T_m) + 2n_s(1 - T_m)^{\frac{1}{2}}}{T_m} \right) \right]^{\frac{1}{2}}, \quad (1)$$

where T_m is the maximum (or minimum) value of transmittance corresponding to the wavelength, n_s the refractive index of the substrate (in our case $n_s = 1.52$ for glass substrate) and $n_{f(1,2)}$ the refractive indices at two adjacent maxima (or minima) at λ_1 and λ_2 . Using $n_{f(1,2)}$ values obtained from (1), thickness of the films d can be determined by the following relation:

$$d = \frac{(\lambda_1 \lambda_2)}{(2(n_{f1} \lambda_2 - n_{f2} \lambda_1))}. \quad (2)$$

The obtained thickness of TiO_2 thin films from the fringe patterns in the transmittance spectrum by (2) are shown in table 1. It is found that film thickness increases proportionally to the B concentrations, which can be explained as follows: Since the ionic radius of B is smaller than the ionic radius of Ti, ionic bonding between boron and oxygen is stronger compared to the ionic bonding between titanium and oxygen. This strong bonding between boron and oxygen reduces the rate of evaporation and results in increase in thickness with increase in doping concentration. On the other hand, 1% B-doped TiO_2 thin film has the same thickness with the pure one due to similarity of the transmittance spectra.

After obtaining the values of d , absorption coefficient (α) can be determined by the following formula:

$$\alpha = -\frac{1}{d} [\ln(T)]. \quad (3)$$

According to Tauc's relation for optical transitions, the photon energy dependence of the absorption coefficient can be described by Tauc (1970):

$$(\alpha h\nu) = A (h\nu - E_g)^r, \quad (4)$$

where A is a constant, $h\nu$ the photon energy, E_g the optical bandgap energy of the material and the exponent $r = 1/2$ stands for the allowed direct transitions, since it gives the best linear graph in the band edge region. Figure 2 illustrates

Table 1. Optical parameters of pure and doped TiO₂ thin films calculated by UV-Vis spectra.

	Pure TiO ₂	1%B:TiO ₂	3%B:TiO ₂	5%B:TiO ₂	7%B:TiO ₂	10%B:TiO ₂
$T_{\max}$ (visible region)	93.72%	93.72%	90.53%	90.66%	88.53%	90.63%
d (thickness)	108 nm	108 nm	130 nm	113 nm	138 nm	164 nm
E_g (energy bandgap)	3.85 eV	3.85 eV	3.93 eV	3.90 eV	3.96 eV	3.98 eV
n (580 nm) (refractive index)	1.67	1.67	2.00	1.89	2.60	3.12
ε_{∞}	2.99	2.99	3.61	4.20	3.57	2.99
N/m^* (cm ⁻³ /gr)	7.42×10^{42}	2.74×10^{43}	1.79×10^{42}	1.72×10^{43}	4.14×10^{42}	7.42×10^{42}

Figure 2. Plot of $(\alpha hv)^2$ vs photon energy (hv) for pure and B-doped TiO₂ thin films.

a plot of $(\alpha hv)^2$ vs photon energy hv for pure and doped TiO₂ thin films. The bandgap energy (E_g) values which can be obtained by extrapolating the linear portion to the photon energy axis are given in table 1. The estimated E_g for pure TiO₂ was 3.85 eV, which is consistent with the reported value for anatase TiO₂ (Park and Kim 2005). The bandgap energy increased with increasing dopant concentration and was estimated to be 3.98 eV at the highest dopant concentration of 10%. This change of ~ 0.13 eV was due to the incorporation of B³⁺ ions into TiO₂ crystal structure and B₂O₃ forming a layer on the particle surface. However, the bandgap value decreases in 5%-doped B doping concentration which may be due to $sp-d$ exchange interactions and big crystallite size ($d > 15$ nm) and has also been theoretically explained using the second-order perturbation theory (Singh *et al* 2009).

In order to calculate the optical constants, the refractive index (n) and extinction coefficient (k) of thin films at different wavelengths, based on an absorbing thin film on a transparent substrate has several orders of magnitude larger than the thickness of the film. The spectrophotometric measurements of transmittance and reflectance measurements were

used. The homogeneous film has thickness d and the complex refractive index, $n^* = n - ik$, where n is the refractive index and k the extinction coefficient, which can be expressed in terms of the absorption coefficient, α by the equation:

$$k = \frac{\alpha \lambda}{4\pi}. \quad (5)$$

The reflectance $R(\lambda)$ as a function of the refractive index, n and the extinction coefficient, k , are given by Fresnel formula as (Banerjee 2005):

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \quad (6)$$

If one solves (6) via elementary algebraic manipulation, refractive index is found as

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - k^2}. \quad (7)$$

Figures 3 and 4 present the extinction coefficient k and the refractive index, n , of the pure and doped thin films as a function of wavelength, respectively. As seen in both figures, the refractive index and extinction coefficient values decrease with increasing wavelength. Therefore, these decrease in the values of refractive index and extinction coefficient with wavelength attribute to the significant normal dispersion behaviour of the films. These observations confirm the decrease in the loss of light due to scattering and absorbance with increase in λ . Additionally, the value of k is close to zero, in agreement with the fact that TiO₂ thin film is transparent in the visible-spectral region. Change in the extinction coefficient at lower wavelengths is caused by the band-to-band excitation as fundamental transition. The obtained values of refractive index at 580 nm are given in table 1. The obtained value of refractive index for pure TiO₂ is found to be lower than that of those obtained before in the literature (Bass *et al* 2009). This may be attributed to the refractive index which is affected by crystallinity, electronic structure, lattice point defects, porosity and/or stresses (Lu *et al* 1997; Alver *et al* 2008).

As shown in table 1 as well as in figures 3 and 4, the refractive index values and the extinction coefficients are influenced by dopant and generally, both of them increase with increasing doping concentrations in the wavelength

Figure 3. Variation of extinction coefficient with wavelength for pure and B-doped TiO₂ thin films.

Figure 4. Variation of refractive index with wavelength for pure and B-doped TiO₂ thin films.

range of 500–600 nm. Furthermore, as clearly seen from the inset of figure 4, refractive index increases with increasing doping concentrations in the wavelength range of 400–1100 nm above the absorption edge. The slight increase in refractive index with increasing doping concentrations can be attributed to an increase in packing density. This is expected because the film porosity decreases with increasing doping

concentrations (Yakuphanoglu *et al* 2005; Sreemany and Sen 2007). Evaluation of the refractive indices of optical materials is remarkably important for applications in integrated optical devices such as switches, filters, modulation, etc. in which refractive index is a key parameter for the device design (Sen *et al* 1988).

The complex dielectric constant, ϵ , components of a material in terms of the optical constants n and k are given as:

$$\epsilon_1 = n^2 - k^2, \quad (8)$$

where ϵ_1 is the real part, while the imaginary part is:

$$\epsilon_2 = 2nk = -\left(\frac{\epsilon_\infty \omega_p^2}{8\pi^2 c^3 \tau}\right) \lambda^3, \quad (9)$$

where ω_p is the plasma frequency, τ the optical relaxation time, c the velocity of photon and ϵ_∞ the high frequency dielectric constant.

The variation of the dielectric constant with λ^2 indicates that some interactions between photons and electrons are produced in this wavelength range. When $n^2 \gg k^2$ and $\omega\tau \ll 1$, the dielectric constant in (8) equals to Spitzer–Fan model (Spitzer and Fan 1957).

$$\epsilon_1 = \epsilon_\infty - \left(\frac{e^2}{4\pi^2 c^2 \epsilon_0}\right) \left(\frac{N_{\text{opt}}}{m_h^*}\right) \lambda^2, \quad (10)$$

where ϵ_0 is the free space dielectric constant and N_{opt}/m_h^* the ratio of free optical carrier concentration (N_{opt}) to the free carrier effective mass (m_h^*). Using the plot of variation of the real dielectric constants with λ^2 shown in figure 5, y-axis intercept for the linear part of curve at higher wavelengths gives the value of high frequency dielectric constant while

Figure 5. Plot of variation of real dielectric constants with λ^2 .

the slope gives N_{opt}/m_h^* ratio. The obtained values of ε_∞ and N_{opt}/m_h^* are also displayed in table 1. It is clear from the table that high frequency dielectric constant, ε_∞ , is effected from doping randomly.

The crystal structure and orientation of thin films have been investigated by X-ray diffraction (XRD) method over the range 20–70°. XRD pattern of TiO₂ thin films doped at different concentrations of B are given in figure 6. XRD results indicate that pure and 1% B-doped TiO₂ thin films were the anatase phase crystal plane with (101) and (211) reflections. When B concentration rises to 3 and 5%, instead of the anatase phase crystal plane (211) reflection, hexagonal crystal structure in TiB₂ phase with (111) reflection has been seen in figure 6. It can be attributed to the result of chemical reaction during the experiment, boron would probably join the lattice as interstitial having single negative charge and caused the formation of TiB₂ phase. For 7% B-doped TiO₂ thin film, cubic crystal structure in B₂O₃ phase and for 10% B-doped TiO₂ thin film, tetragonal crystal structure

in TiB_{0.024}O₂ rutile phase were observed corresponding to (310) and (110) reflections, respectively.

The intensity of all anatase peaks were found to be lesser compared to pure TiO₂ on increasing the concentration of B dopant, intensity of the anatase peaks was further decreased and for 10% B-doped TiO₂ thin film, it disappeared. The decrease in peak intensities is basically due to replacement of Ti and O ions with B ions.

The crystallite size of TiO₂ thin films can be deduced from XRD-line broadening using the Scherrer's formula (Cullity 1978):

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (11)$$

where D is the crystallite size (nm), λ the wavelength of CuK α radiation (nm), θ the Bragg angle and β the full width at half-maximum (FWHM) of diffraction peak. Furthermore, it is seen that crystallite size of thin films varies randomly in the range of about 16.2–27.4 nm and thus forms nanosized films.

Figure 6. XRD spectra of pure and B-doped TiO₂ thin films at 500°C annealing temperature.

Figure 7 shows FE-SEM micrographs of pure and B-doped TiO_2 thin films. As clearly shown in figure 7 all films have homogeneous surface morphology. All the films are compact, dense and adhere well to the substrates. The surface properties of TiO_2 thin films seem to change significantly as a function of doping concentrations. While the pure film

has some voids which disappeared gradually by increasing B concentrations. The grain size for all samples is of the order of nano and the grain morphology is irregular. Pure (a) and 1% (b) B-doped TiO_2 thin films have bigger grains in size than other samples. Therefore, in this study it is clear that B plays an important role in decreasing the grain size of TiO_2 .

Figure 7. FE-SEM images of pure (a), 1% (b), 3% (c), 5% (d), 7% (e) and 10% (f) B-doped TiO_2 thin films at 50,000 $\times$ magnification.

4. Conclusions

Influence of boron doping on the optical and structural properties has been reported for TiO₂ thin films at different doping concentrations. All the nanostructured pure and boron doped TiO₂ thin films have high transparency of over 88%. The direct optical bandgap of the films was found in the range of 3.85–3.98 eV, as the doping concentration is increased. Obtained optical parameters such as extinction coefficient, refractive index, dielectric constant, high frequency dielectric constant and N_{opt}/m_h^* ratio indicate that doping of TiO₂ by B at 1% concentration rate has no effect on pure thin film. To enhance the optical properties of TiO₂ thin films, it has to be doped at higher rates than 1%. Structural investigations showed that crystalline of these thin films changed randomly with increasing B concentrations. XRD pattern of pure and 1% B-doped TiO₂ thin films are found to have a polycrystalline nature oriented along (101) and (211) planes. The presence of other orientations such as (310), (110) and (111) were also detected with higher B concentrations. It can be attributed that these phases have been formed as a result of chemical reaction during the deposition process. From the surface analyses, it was determined that TiO₂ has relatively smooth morphology and smaller particles, which are well connected to each other. Also, it strongly adheres to the substrates and has tightly bounded particles. The variations of structural, morphological and optical properties were observed depending on the dopant materials, as a consequence, boron doping to TiO₂ structure shows promise on a more suitable material than other dopants currently being used in optoelectronic device technology.

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