Optical Band Energy, Urbach Energy and Associated Band Tails of Nano Crystalline TiO\textsubscript{2} Films at Different Annealing Rates

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Abstract: Increase in world population has led to more energy demand. Therefore, there is need for utilization of green and renewable energy. Dye sensitized solar cells (DSSCs) based on TiO\textsubscript{2} have attracted a lot of attention as an alternative source as compared to current silicon technology. In this study, TiO\textsubscript{2} thin films were deposited on doped fluorine tin oxide layer (FTO) glass substrates using sol-gel doctor blading technique. The films were annealed at different rates (1step, 2°C/min and 1°C/min) up to a temperature of 450°C followed by sintering at this temperature for 30 minutes. UV-VIS spectrophotometry was employed to probe the absorbance and reflectance of the films. It was found that, the optical parameters, such as the reflectance, the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of dielectric constant, skin depth, Urbach energy and the energy gap; all depend on the annealing rate. The skin depth for the samples in visible region were found to increase from $6.319 \times 10^{-5}$ to $11.968 \times 10^{-5}$ cm$^{-1}$ due to annealing. The Optical band energy (Eg) decreased from 5.04eV for as deposited film to 4.35eV at annealing rate of 1°C/min for direct allowed and from 2.76 to 2.56 eV for indirect transitions. Urbach tails in weak absorption region decreased with annealing rate. Urbach energies (Eu) were in the range of 432-505 meV for as deposited and annealed films. This was used to account for the disorder of the films. An inverse relation between Urbach energy and optical band energy as result of annealing rate was reported.

Keywords: Annealing Rate, Band Gap, Skin Depth and Urbach Energy

1. Introduction

Titanium IV oxide (TiO\textsubscript{2}) in the recent decades is attracting much attention to many researchers due to its excellent chemical, thermal, optical and electrical properties. TiO\textsubscript{2} extensive investigations is due to its uses in various fields such as gas sensors [1], electronic materials [2], wet-type solar cells [3], electrochromic systems [4], antireflective coatings [5] and dye-sensitized solar cells [6]. TiO\textsubscript{2} in nature occurs in the structure of anatase, rutile and brookite [7]. The anatase phase can be obtained at temperatures below 800°C, which at higher temperatures transform to the more stable rutile structure [8]. The surface morphology is strongly affected by the annealing temperatures of TiO\textsubscript{2} thin films. The thin films have high transparency in the visible range and high opacity in the UV region [9]. The layer thickness of TiO\textsubscript{2} decreases with increase in annealing temperature attributed to densification of the titanium dioxide layer and evaporation of the carbonaceous material and absorbed water [9]. The highest refractive index obtained for anatase TiO\textsubscript{2} is 2.26 which increases to 2.57 with further annealing. This can be explained by crystalline structure development [10]. UV-VIS studies on optical absorption properties of TiO\textsubscript{2} has shown sharp absorption edges in the UV region and the absorption varying with annealing temperature. The absorption edge (in anatase) annealed at 450°C showed a red shift into the visible region [11]. The UV absorption peaks in
TiO$_2$ occurs due to band to band absorption [12, 13]. The hump in the visible region has been attributed to presence of Ti$^{3+}$ or oxygen vacancies [14, 15] that bring about defect complex and form color centers [16, 17]. The band gap of TiO$_2$ films lowers with increase in annealing temperature which is associated with presence of defect bands in the band gap. An absorption tail (Urbach tails) is produced by these defect states which extends deep into the forbidden gap and the associated energy is the Urbach energy [18, 19].

The physical and chemical properties of the prepared materials depend very much on the technique applied for their fabrication. Preparation of TiO$_2$ thin films have been done using many techniques, which includes, cathodic electrodeposition [20, 21], Pulsed laser deposition [22], Mist plasma evaporation [23], electron beam evaporation [24], Metal organic chemical [25]. Doctor Blade is the most popular approach because it is simple, easy to scale up, cost effective and suitable for a large area processing [26]. UV – visible spectrophotometry has been used to characterize nanocrystalline TiO$_2$ thin films [27]. Optical measurements such as Reflectance and absorbance have been analysed using Scout software [28]. Optical band gap, Eg is calculated using Tauc’s plot using absorption coefficient data obtained from scout software [29, 30]. Urbach energy and weak absorption tail energy is determined using absorption coefficient data [31]. In this work, allowed direct and indirect band gap, Urbach energy and associated Urbach tails were studied at different annealing rates.

2. Experimental Procedure

TiO$_2$ thin films were deposited on FTO (SnO$_2$: F) 7 Ω/sq, (Xinyan Technology Co. Limited, China) glass substrates using sol-gel technique. The TiO$_2$ (T/SP, 18% wt, 15-20nm was sourced from Solaronix, Switzerland) The prepared films were annealed at different rates using muffle furnace. The temperature was increased gradually at the up to 450°C followed by sintering for 30 minutes which is one step annealing. The other annealing rate was 1°C/minute where by the temperature was raised at a rate of 1 degree Celsius per minute up to 450°C followed sintering for 30 minutes, similar procedure was repeated for 2°C/minute annealing rate. The optical reflectance and absorbance were measured in the wavelength range of 300-800 nm using double beam UV-Visible spectrophotometer (Shimadzu UV probe 1800, Japan). Values of absorption coefficient for all corresponding wavelength were obtained using SCOUT analysis [28]. Direct and indirect allowed optical band gaps were modelled using Tauc’s relation [29]. Urbach energy and tails were obtained from absorption coefficients [31].

3. Result and Discussion

3.1. Reflectance

Figure 1 shows reflectance versus wavelength spectra for annealed TiO$_2$ films.
3.2. Absorbance and Absorption Coefficient

Figure 2 (a) shows the absorbance and 2 (b) the absorption coefficient spectra in the range of 200-800 nm for TiO$_2$ thin films for as deposited and annealed. In the wavelength range of 250 nm to 380 nm, there is a significant increase in absorbance with decrease in annealing rate, this is due to high absorption of TiO$_2$ films in the ultraviolet region. Beyond a wavelength of 400 nm, the absorbance is fairly low and constant whereas the absorption edge tails are exponential, signifying the presence of localized states in the energy bandgap. The magnitude of tailing can be projected by plotting the absorption edge in terms of Urbach equation [32]. In the exponential edge region, the absorption edge provides a measure of the energy bandgap and the exponential tails dependence of the absorption coefficient [33, 34]. Therefore, lowering annealing rate leads to a reorganization and distribution of states from band to tail which is attributed to the improvement of crystallinity [18, 19].

The $\varepsilon_1$ and $\varepsilon_2$ represent the amount of energy stored in dielectrics as polarization and loss energy respectively. Dielectric constants of annealed films were lower than that of as prepared. Real part dielectric increase with decreasing annealing rate and decreases with increasing wavelength. Imaginary part decreases sharply between 200nm to 400nm and remains fairly constant for all other wavelengths >400nm.

A greater ratio of $\varepsilon_2$ to $\varepsilon_1$ shows a very good low-loss dielectric of the thin film coatings having nature in the frequency range of interest. This is attributed to the intensification in the electron density of the films [35]. In general, the enhancement in crystallinity due to annealing of the films decreases the degree of electron scattering and thus increase the free-electron density [36, 37].

3.3. Dielectric Constants

Figure 3 (a) and (b) represents the relationship between real and imaginary dielectric constants with wavelength for TiO$_2$ thin film for various annealing rates. They were calculated from equations (1) and (2).

\[
\varepsilon_1 = n^2 - K^2 
\]  

(1)

\[
\varepsilon_2=2nK
\]  

(2)

\[
x = \frac{\lambda}{2\pi k}
\]  

(3)

Figure 4 shows a plot of skin depth versus wavelength. It can be seen that at shorter wavelengths less than 500nm there is no significant change in skin depth values. This is due to equal probability in absorption in this region.

However, after wavelength, $\lambda$ (cut off) (~525nm) the skin depth decreases for as deposited and annealed films whereas as deposited film has the lower skin depth values and film with lower annealing rates (1°C/min and 2°C) has higher values. The skin depth peaks for as prepared, 1 step, 2°C/min and 1°C/min were as shown in table 1.

| Annealing rate | Peak wavelength | Skin depth ($10^{-5}$) (m$^{-1}$) |
|---------------|----------------|-----------------------------------|
| As prepared   | 591            | 6.319                             |
| 1 step        | 655            | 10.164                            |
| 2°C/min       | 664            | 11.968                            |
| 1°C/min       | 713            | 11.772                            |
3.5. Direct Allowed and Indirect Allowed Optical Band Energy

The optical band gap energy, \( E_g \) was obtained from the absorption coefficient, \( \alpha \) through Tauc’s relations 4 and 5 for direct and indirect transitions [38, 39].

\[
\alpha h\nu = B_1(h\nu - E_{g1})^2 \\
\alpha h\nu = B_2(h\nu - E_{g2})^{\frac{1}{2}}
\]

where \( B_1 \) and \( B_2 \) are constants, \( \alpha \) is the absorption coefficient, \( h\nu \) is the photon energy and \( E_{g1}, E_{g2} \) are the direct and indirect band gaps, respectively. Figure 5 (a) and 5 (b) show the representation of the dependence of \( (\alpha h\nu)^2 \) and \( (\alpha h\nu)^{\frac{1}{2}} \) respectively upon photon energy for as deposited and annealed TiO\(_2\) films at different rates.

\[\text{Figure 5. (a) The variation of the } (\alpha h\nu)^2 \text{ with the photon energy and (b): The variation of } (\alpha h\nu)^{\frac{1}{2}} \text{ with increasing photon energy of TiO}_2 \text{ thin-film samples at different annealing rates.}\]

Figure 5a shows the experimental data of a plot of \( (\alpha h\nu)^2 \) versus photon energy linear fit was extrapolated and the intercept determined the optical direct band gap, \( E_{g1} \). The optical allowed direct band gap energies were found to decrease from 5.04 to 4.35 eV for the present annealed TiO\(_2\) films. While for indirect allowed band gap, \( E_{g2} \) extrapolation of the linear portion of the plot \( (\alpha h\nu)^{\frac{1}{2}} \) versus photon energy decreased from 2.76 to 2.56 eV. These values are in good agreement with the data obtained for like phase [38-40]. It was further found that this decrease in \( E_g \)-values is as a result of the improvement of the crystallinity of films as well as the structure and the surface morphology of samples [41]. In the present work, the decrease in optical band gap is attributed to the oxygen defect band states formed in the band gap and increase of oxygen vacancies in the crystal lattice.

3.6. Urbach Energy (\( E_u \)) and Band Edge Absorption Tails

When a disorder arises during transition of electrons from top valence band to the bottom of conduction band, electrons encounter density of their states \( \rho (h\nu) \), where \( h\nu \) is the photon energy which result to tailing into the energy gap. This tail of \( \rho (h\nu) \) extending into the energy band gap is referred to as Urbach tail. Consequently, the energy associated with this tail is referred to as Urbach energy \( (E_u) \) which is due to tailing of absorption coefficient \( \alpha (h\nu) \) in an exponential manner. Urbach energy is calculated as in equation 6:

\[
\alpha (h\nu) = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right)
\]

Where \( \alpha_0 \) is a constant, \( h\nu \) is the photon energy and \( E_u \) is the Urbach energy.

In Figure 6, Region W represents the weak absorption region for as deposited and annealed TiO\(_2\) films, U represents the urbach region and T represents the optical transitions from one extended state to another extended state. It is observed that all samples have an associated Urbach tail in region W.

The urbach tailing was observed to decrease with decrease in annealing rate, urbach tail of as prepared films is longest and that of 1degree/min annealing rate is the shortest. From literature, exponential tails are associated with low crystalline films, and disordered amorphous materials because of localized states [42, 43]. Therefore, it is evident that the energy below approximately 2.5eV is not sufficient to initiate a interband transition of electrons resulting to urbach tails in region W (weak absorption region).

\[\text{Figure 6. In (a) vs (h\nu) for TiO}_2 \text{ thin films before and after annealing at different rates.}\]

Earlier work has associated this tailing of bands to lattice vibration due creation of sub-surface defects such as vacancies, vacancy-interstitial pairs and antisites [44]. We therefore,
attribute the tailing of bands to formation of oxygen vacancies due to annealing, whereas decrease in urbach tailing with decrease in annealing rate is due to improvement in crystallinity of the films. Urbach energy ($E_u$) was estimated by plotting $\ln (\alpha)$ vs photon energy ($h\nu$) and fitting the linear portion of the curve with a straight line as shown in figure 7. From equation 6 reciprocal of the slope of the linear region yields the value of $E_u$. Estimated Urbach energies of TiO$_2$ films as deposited, 1 step, 2deg/min and 1 deg/min were 432meV, 464meV, 454meV and 505meV respectively. The values of urbach energies were correlated with optical band energies as shown in figure 8.

We observe from figure 8 an increase in $E_u$ from as prepared TiO$_2$ film to 1 step annealing rate followed by a decrease for 2 deg/min rate and an increase again at 1deg/min rate. Based on literature, the effect of annealing process on structural and optical properties has been studied [45]. XRD analysis by Shomara et al shows increase in annealing temperature gradually increases crystallite sizes, decreases lattice imperfections as well as enhancing nucleation and coalescence. However, localized tail states in amorphous semiconductors have been reported to arise from defects generated disorder. Increase in substrate temperature was also found to decrease associated $E_u$ due to shuffling motion of atoms in randomly stacked polyhedra in an amorphous matrix. [42, 46]. As the temperature of the substrate increases, films were found to be more crystalline with increased band gap and reduced Urbach tail. Therefore, as observed in figure 8, all annealed films have a higher $E_u$ than as prepared film which can be attributed to presence of localized states in annealed films. Decrease in $E_u$ from 464meV to 454meV can be attributed to shift of films from amorphous to microcrystalline whereas the increase in Eu 454meV to 505meV at low annealing rate (1 deg/min) could be due creation of oxygen vacancies due to absorption in form of lattice vibrations. It has been reported a decrease in of optical band gap, $E_g$ with the increase in annealing temperature [47]. Increased levels of localized states near conduction band and valence band is as a result of annealing [48]. These levels are ready to receive electrons and generate tails in the optical energy gap. Decrease in energy gap can be attributed to the increased size of particles in the films. Hence, we can associate the decrease in the band gap energy, $E_g$ with the increase in annealing temperature.

Earlier studies on the effect of annealing temperature on structure, microstructure, morphology and optical properties of TiO$_2$ thin films revealed a nanocrystalline structure, uniform surface morphology and decreasing optical band gap with increasing annealing temperature [49]. As deposited TiO$_2$ films were found to be amorphous. The crystallinity of the tetragonal anatase phase improved after annealing at $T \geq 693K$ [49]. The change from amorphous-to-polycrystalline nature has been reported to occur after annealing at about 400°C.
Band gap of the film decreased from 3.4 to 3.32 eV after annealing at 600°C [50]. A decrease in transmittance and optical energy band gap was reported with an increase in annealing temperature [51]. Studies on anatase TiO$_2$ thin films deposited by chemical bath deposition, revealed that increasing annealing temperature lead to improvement of the crystallinity quality of the films, increasing the urbach energy and the reduction of the band gap value [52].

4. Conclusion

TiO$_2$ thin films have been deposited using doctor blading technique and characterized using UV-VIS NIR spectroscopy. A stout dependence of reflectance, the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of dielectric constant, skin depth, Urbach energy and the energy gap on annealing rate has been established. Variations in optical parameters have been associated from literature with changes in microstructure at different annealing rates giving rise to significant decrease in optical band-gap and increase in Urbach energy. Sub-surface defects of the films as manifested by the Urbach energy tails in the band-gap, and increase in Urbach energy. Sub-surface defects of the films as manifested by the Urbach energy tails in the band-gap, and increase in Urbach energy. Sub-surface defects of the films as manifested by the Urbach energy tails in the band-gap, and increase in Urbach energy. Sub-surface defects of the films as manifested by the Urbach energy tails in the band-gap, and increase in Urbach energy.

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