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Correlation of Bond Energy and Optical Band Energy of Annealed TiO_2 Thin Films

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Abstract We report on the correlation between bond energy and optical band energy of TiO_2 thin films prepared through sol gel doctor-blade technique. The TiO_2 films were deposited on doped fluorine tin IV oxide (SnO_2:F) layer on glass substrates. UV-Vis-NIR spectroscopy was carried out on as-deposited and subsequent annealed films at different rates from room temperature up to 450°C. The average optical transmittance within the visible region was 73.5%, 73.4%, 70.5% and 69.9% for the as-deposited, 1-step annealed, 2°C/min, and 1°C/min films, respectively. FTIR spectroscopy confirmed presence of functional elements of Ti = O with a peak at 587.7 cm^{-1}. Bond energy for the films was calculated using Madelung equation with inclusion of the second coordination sphere for crystalline state. The values of bond energies were found to be 3.99 eV, 4.02 eV, 4.12 eV and 4.16 eV for the as-deposited, 1-step annealed, 2°C/min, and 1°C/min films respectively. The analysis of the band gap was done using Tauc's relation. Band gap energy ranged from 4.02 eV to 5.04 eV. A statistical correlation between bond energy and optical band energy was established. Films annealed at 1°C/min recorded the highest bond energy and lowest band gap energy. This is attributed to the process of nucleation and crystal growth which are governed by thermodynamic properties. Prolonged exposure to higher temperatures through low annealing rates led to formation of films with high bond energy and low band gap.

Keywords: *bonding energy, optical band energy, annealing rate, TiO_2*

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1. Introduction

Titanium dioxide (TiO_2) has demonstrated wide applications, leading to massive investigation over the recent past decades [1]. Due to the chemical stability, high refractive index and wide optical band gap, TiO_2 films have extensively been used in a number of applications such as Photocatalytic layers [2], dye-sensitized solar cells [3], Optics industry [4], dielectric applications [5] and self-cleaning purposes [6]. The tetrahedral anatase, rutile and orthorhombic brookite are the three crystal phases of TiO_2 [7] evident that it has wide range of applications. Optical properties of TiO_2 characterized by UV-visible spectrophotometry show an average transparency of approximate 70% [7]. TiO_2 is well known to be a n - type semiconductor having a wide indirect energy band gap [6,8]. The anatase phase is highly attractive in titanium oxides coatings due to its low extinction coefficient and high refractive index [9]. Studies have shown that annealing temperature influences the optical and structural properties of TiO_2 films [10]. The surface roughness/morphology of TiO_2 thin films was found to be influenced by annealing, 1°C/min being more smooth and homogenous due to enhance mobility of molecules [11].

Various deposition methods have been used to grow TiO_2 thin films; these are electron - beam evaporation [12], DC reactive magnetron sputtering [13], chemical vapor deposition [14] and doctor blade technique [15]. Doctor blade is widely used for its ease, large area deposition, low cost, thickness control and good uniformity [11,16].

Scout software has been used in analysis of optical measurements such as transmittance and reflectance [17]. Tauc's relation utilizes absorption coefficients to model optical band gaps [17]. Both direct and indirect allowed optical band gap of TiO_2 films are influenced by annealing [18].

Fourier Transform Infrared Spectroscopy (FTIR) technique is used to identify vibrational modes of bonds and functional groups. [19]. Bond energies in oxide compounds are the main factor determining structure and properties of substances. The bond energies in the components of the solid phase have been calculated from the Madelung equation [20].

In this study TiO_2 films were coated on FTO substrate. The films were annealed at different rates. A correlation of bond energy and optical band energy as a function of heat treatment was established.

2. Experimental Procedure

FTO glass substrates (SnO_2: F) of sheet resistance, 7 Ω/sq, (Xinyan Technology Co. Limited, China) were cleaned using standard procedure by use of acetone (99.5%), ethanol (purity 99.5 %,) and deionized water all sourced from Sigma-Aldrich Chemicals company. The substrates were dried with pressurized hot air and then stored in special boxes ready for deposition.

Nanocrystalline TiO_2 (T/SP, 18% wt, 15-20nm, sourced from Solaronix, Switzerland) was coated on FTO (SnO_2:F) glass substrates using sol-gel doctor-blading technique. In order to enhance homogeneity, the films were dried at ambient condition for 25 minutes. Freshly prepared samples were annealed at different rates using Muffle furnace. At one step annealing rate the temperature was raised from room temperature to 450°C and sintered at that temperature for 30 minutes. At 2°C/minute annealing rate temperature was raised gradually in steps of 2°C every minute up to 450°C followed by sintering for 30 minutes. At 1°C rate temperature was raised by 1 degree centigrade every minute up to 450°C and then sintered.

Optical transmittance and reflectance of the samples was done using UV-VIS spectrophotometer for the wavelength in the range 300 to 1100nm. The optical parameters (refractive index, extinction coefficient and absorption coefficient) were obtained by performing a best fit of transmittance spectrum, using commercial SCOUT software [17]. That is based on the transfer matrix method [17]. The SCOUT software generated the theoretical transmittance spectrum of TiO_2 films, calculating its effective absorption coefficient using extinction coefficient function. The optical band gap was determined using Tauc's equation [17,18].

Fourier transform infrared spectroscopy was done on the samples. Infrared as a function of frequency was subjected to the samples and absorption and transmittance spectra obtained.

Values of vibrational frequency for $Ti = O$ bond for each sample were obtained from the absorbance as a function of wave numbers spectra. Bond energy (E) at different annealing rate was calculated using Madelung equation.

3. Results and Discussion

3.1 Transmittance and Reflectance

Figure 1 shows transmittance spectra for various annealed samples. The transmittance spectra cluster together for the wavelength range considered. Samples annealed at the lowest annealing rate had the lowest transmittance across the considered spectrum. This shows that the sample annealed at 1°C/min has the highest absorbance. This can be attributed to increased rate of evaporation of oxygen during the process of annealing [18]. The visible region is characterized by higher transmittance above 70%. The transmittance decreases sharply as wavelength reaches the UV region.

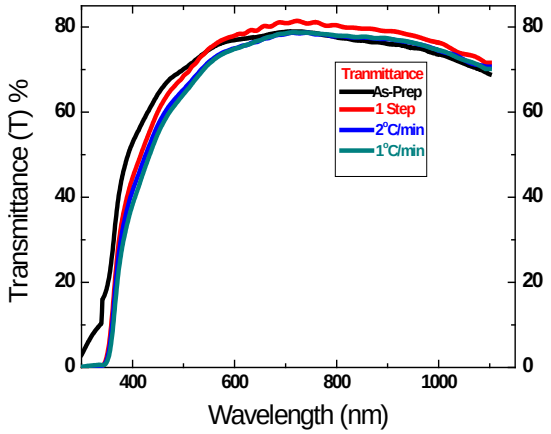

Figure 1. Transmittance spectra of annealed TiO_2 films

Figure 2 shows reflectance spectra for films annealed at different annealing rates. The visible region is characterized by low reflectance below 30%. The spectra exhibit similar trend with transmittance of clustering together over the considered region. Change in optical constants as the films are annealed leads to sharp decrease in reflectance within the visible region [18]. Surfaces of the films treated to low annealing rates are more smooth and homogenous due to enhanced mobility of molecules [21]. A slight increase in reflectance within the IR region was noted.

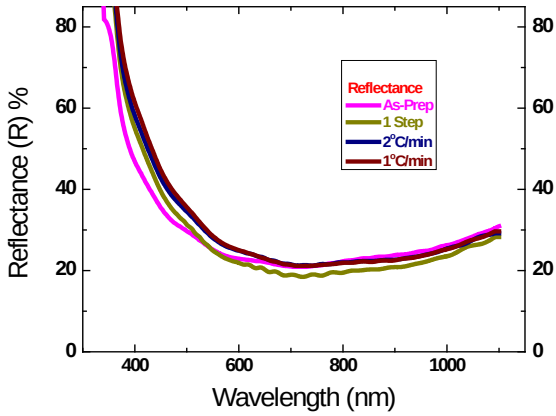

Figure 2. Reflectance spectra of annealed TiO_2 films

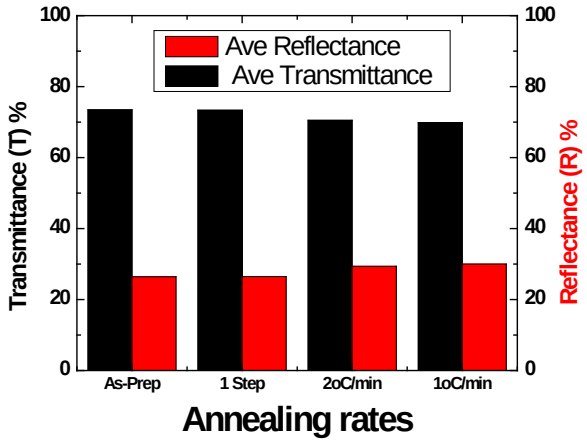

Figure 3. Average transmittance and reflectance in the visible region of annealed TiO_2 films

Figure 3 shows the average transmittance of all the films in the visible region. The as deposited films show a higher average transmittance than the annealed. The film annealed at 1°C/min has the lowest transmittance. It has been reported that transmittance decreases with increase in annealing temperature. This is due to low surface roughness that is associated with the scattering of light and increase in packing density and crystallinity of the films [18]. Further, increase in light diffusion with the crystallite size and particle aggregation was also found to influence transmittance [18]. In this work, the decrease in transmittance and increase in reflectance due to decrease in annealing rate can be attributed to surface morphology, crystallite size and particle aggregation.

3.2. Absorption Coefficient

The values of absorption coefficient α were evaluated from high absorption region at the fundamental absorption edge of the annealed films. Plots of absorption coefficient versus wavelength are shown on Figure 4. It is observed that the absorption coefficients for all the samples are in the order of 10^4 cm^{-1}. Absorption coefficients are also seen to increase sharply with increase in photon energy. There is a decrease in absorption coefficient with a decrease in annealing rates.

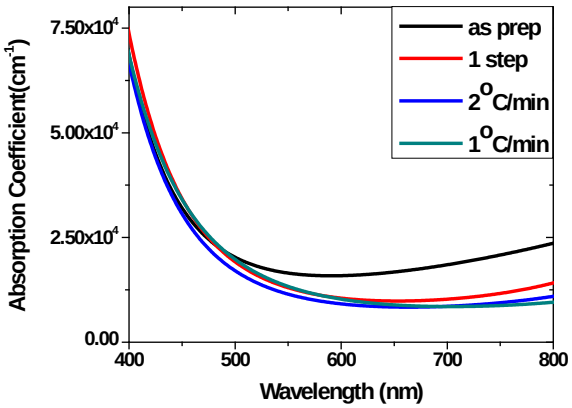

Figure 4. Absorption coefficient versus wavelength spectra

Absorption coefficient is mainly influenced by fundamental absorption and scattering losses. At short wavelength, scattering losses is negligible [22]. This may be due to the increase in film homogeneity with increase of surface roughness promoting the increase of surface scattering of the light [22] Hence, the decrease in absorption coefficient with decrease in annealing rates can be attributed to low absorption and high scattering losses of the films.

3.3. Optical Band Energy

Contribution of scattering losses in the shorter wavelength is negligible and at higher absorption region, the absorption coefficient contributes significantly to the band gap of the material [22]. In high absorption region ($\alpha > 10^4$ cm^{-1}) the optical band energy can be determined by Tauc's equation 1 [17].

$$h\nu\alpha = A(h\nu - E_g)^{\frac{1}{2}} \quad (1)$$

Where, E_g is the material energy band gap, A is the energy dependent constant, h is the planks constant, v is the frequency and α the absorption coefficient. Figure 5 shows a plot of $(h\nu\alpha)^2$ versus photon energy. The band gap energies of the samples were obtained by fitting a linear line and the regression of each linear fit was estimated from intercept of photon energy axis as shown in Figure 5. The values obtained were 5.04 eV, 4.74 eV, 4.4 eV and 4.35 eV for the as-deposited, 1-step annealed, 2°C/min, and 1°C/min films, respectively. Optical Band energies of annealed films were lower than the as deposited. It has been observed that increase in grain size of TiO_2 with annealing lead to a decrease in optical band gap [23]. The excitation of valence band and conduction band to receive electrons due to lower annealing rate led to generation of tails in the optical energy gap hence reducing the band gap energy [23].

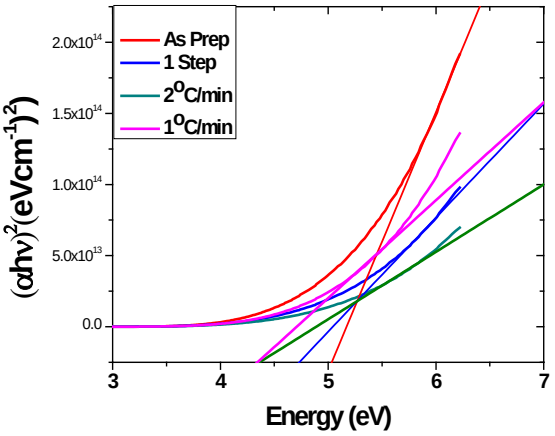

Figure 5. A plot of $(h\nu\alpha)^2$ against photon energy for annealed TiO_2 films.

The decrease in optical band energy is attributed to improvement of microstructure and crystallinity. The optical band gap obtained has been correlated with bond energy discussed in the following section.

3.4. FTIR Analysis and the Bond Energy

The bond configuration of TiO_2 thin film was analyzed by FTIR in the wavenumber range from 400 to 4000 cm^{-1} for as-deposited films and films annealed at different rates. It has been reported that the FTIR spectrum of as-deposited TiO_2 film exhibits a strong, broad absorption band in the region 400-800 cm^{-1}. The presence of a broad band in this region corresponds to the formation of Ti - O and Ti = O bonds in the solutions and to the development of the titanium dioxide network in the films [24].

Figure 6 shows FTIR spectra of absorbance versus wave number for the various films treated at different heat conditions from 500 - 700 cm^{-1} wavenumbers. The absorbance shows a gradual increase with wave number where vibrational peaks occurred between wavenumbers 575 - 600 cm^{-1}. In Figure 6, it is noted that all the samples had sharp vibration peaks occurring at the same wavenumber. Ti = O bond stretch was singled out at 587.7 cm^{-1}. This is in agreement with calculated value from equation 2;

$$\upsilon = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad (2)$$

where μ is the reduced mass of atoms forming the bond and k is the proportional force constant. To confirm these trends, analysis using transmittance spectra was done as shown in Figure 7 and found to be consistent with that of absorbance.

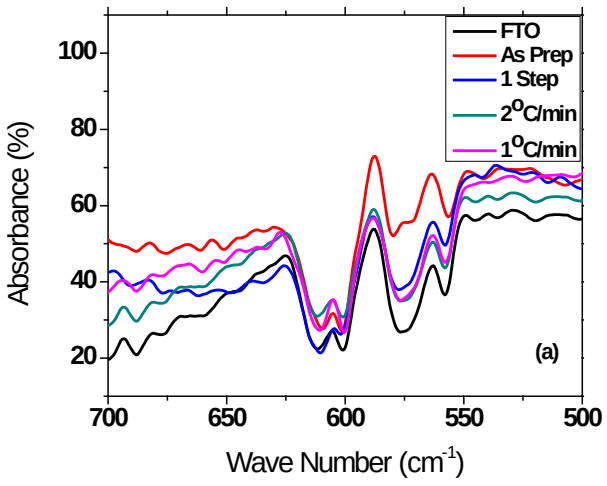

Figure 6. FTIR scatter of absorbance at different wave number.

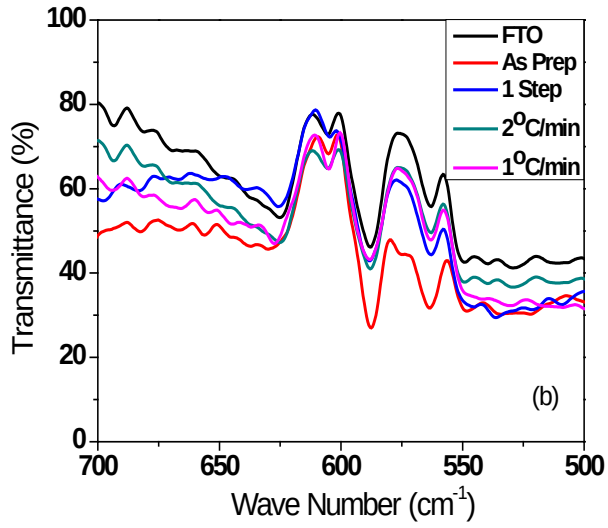

Figure 7. FTIR scatter of transmittance at different wave number.

In 6, IR absorption at 587.5 cm^{-1} peak by the samples varied depending on heat treatment. The absorbance for the as prepared, 1 step, 2°C/min, 1°C/min were 72.6%, 58.9%, 53.1%, and 56.5% respectively. In order to calculate the bonding energies for our films, it was expedient to use the Madelung equation 3 [20];

$$E = \frac{332Mk}{R_o} \quad (3)$$

Where, M is the Madelung constant and k the repulsion coefficient. The value of bond length R_o of as prepared TiO_2 film was calculated from equation 4;

$$R_O = \sqrt{\frac{h}{8\pi^2 C\mu\beta}} \quad (4)$$

Where, C is speed of light, μ is the reduced mass and β vibrational frequency. Proportionality of the absorbance was used to calculate R_o of the annealed films. Computed values of bond energies were 3.99 eV, 4.02 eV, 4.12 eV and 4.16 eV for the as-deposited, 1-step annealed, 2°C/min, and 1°C/min films, respectively. These calculated values of bonding energies were compared to optical band energies from UV - Vis spectroscopy as shown in Figure 8.

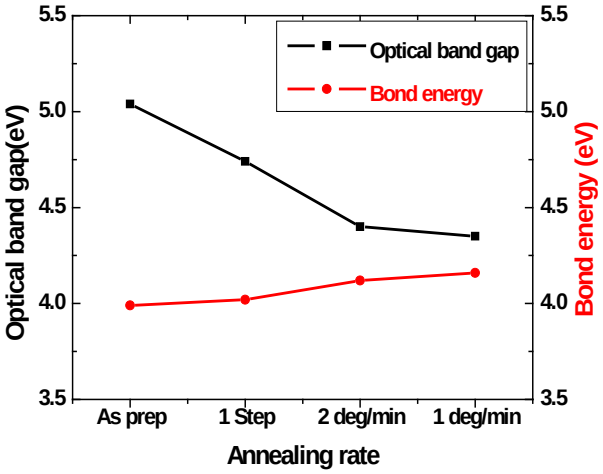

Figure 8. Correlation between band gap and bond energies at different annealing rates

We observe in Figure 8, a decrease in optical band energy as annealing rate is decreased. The film with the lowest annealing rate (1°C/min) has the lowest optical band energy (4.35 eV). Consequently, there is a slight increase in bonding energy with decrease in annealing rates. This shows that both optical band gap energy and bonding energy are affected by variation in annealing rates. Structural analysis shows that as deposited TiO_2 films are mainly amorphous, and after annealing the resulting structures transit to polycrystalline [15,25]. XRD analysis also showed that the structural orientation corresponds to anatase phase for TiO_2 films annealed at 400 - 600°C [15]. Crystallite size and films thickness increase gradually with annealing temperature due to the decrease in concentration of lattice imperfections and enhancement of nucleation and coalescence [15,25]. The optical band gap value of the TiO_2 thin films decreased from 3.95 to 3.65 eV with the annealing temperature increment as a result of the improved crystalline structure [18,25]. The decrease in optical band energy as shown in Figure 8 is attributed to phase transformation from amorphous to anatase occurring during the annealing process, increases in grains sizes as TiO_2 nanoparticles coalesce, decrease in dislocation density and increased localized states near valence band and conduction band.

Structural similarity between a models of amorphous TiO_2, obtained by ab initio molecular-dynamics, and the B-TiO_2 crystalline polymorph has been studied [18]. It is also well established that if dislocation density is high, it causes dilation in the spacing of atoms, which in turn influences the optical band gap of materials. An increased value of dislocation density suggests a higher band gap of the material [23]. Statistical analysis of several experimentally obtained crystalline Ti-O bond-lengths confirms that

crystalline TiO_2 bonds are slightly stronger than the equivalent amorphous bonds [24,26]. Therefore, we associate the slight increase in bond energy to the different bond dissociation energy as the crystallinity is achieved and decrease in bond lengths of TiO_2 due to different annealing rates. Further, annealing rate alters the grains sizes hence TiO_2 nanoparticles coalesce resulting to shorter bond lengths leading to slightly higher bond energy.

4. Conclusion

We have shown that the bond energy and the optical band energy of TiO_2 films vary with annealing rates. The film of as deposited has the lowest bond energy while that of 1°C/min annealing rate has the highest bond energy of 401 kJ/mol. The variations of these energies are affected by TiO_2 phase transformation, changes in dislocation density, grain sizes and bond length. Increase in bond energy confirms a more crystalline structure. The results in this research significantly apply in dye-sensitized solar cells. The efficiency is known to depend on the microstructure and optoelectronic properties of TiO_2.

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