TiO\textsubscript{2} thin films by ultrasonic spray pyrolysis

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Abstract. Titanium dioxide (TiO\textsubscript{2}) thin film have attracted wide interest as photovoltaic, dielectric and photocatalytic material. In this study, the ultrasonic spray pyrolysis method was used to fabricate TiO\textsubscript{2} thin films because of its low-cost operation, absence of vacuum system and convenience of use. The films were sprayed from solution containing titanium(IV)isopropoxide, acetylacetone and ethanol onto microscopy glass and n-type Si(100) substrates at temperatures of 200 to 500 °C. The resulting films were annealed at 500 °C and 700 °C for 1 hour in air. In the present study, optical, structural and electrical properties of produced TiO\textsubscript{2} thin films were investigated as a function of deposition temperature. TiO\textsubscript{2} films deposited ≤ 400 °C show optical transmittance of ca. 80% in the visible region. The band gap of TiO\textsubscript{2} films decreased from 3.52 to 3.25 eV as the deposition temperature increased from 200 to 500 °C. As-deposited films prepared below 500 °C were amorphous, whereas crystalline anatase films were obtained at 500 °C. Further annealing at 700 °C in air led to anatase crystalline formation when films were deposited below 500 °C whereas the films deposited at 500 °C consist of anatase and rutile phases.

1. Introduction
Titanium oxide (TiO\textsubscript{2}) is one of the most important semiconductor oxides. Since the first report by Fujishima and Honda (1972) on the photolysis of water by TiO\textsubscript{2} [1], numerous studies in the properties of nanocrystalline TiO\textsubscript{2} have been generated due to their promising applications in photocatalysis [2], photoelectrolysis [3], dye-sensitized solar cells [4] and gas sensors [5], etc.

TiO\textsubscript{2} belongs to the family of transition metal oxides. It is known that TiO\textsubscript{2} has three polymorph phases: anatase, brookite, rutile [6]. Anatase and rutile have a crystalline structure that corresponds to the tetragonal system while brookite has an orthorhombic crystalline structure [7]. Rutile phase is thermodynamically stable at high temperatures. The anatase phase is metastable and transforms irreversibly to rutile at elevated temperatures [8]. The brookite phase is the rarest of the natural TiO\textsubscript{2} polymorphs and is the most difficult phase to prepare in the laboratory [9]. Anatase phase has a band gap of 3.2 eV, while the rutile phase has a smaller band gap of 3.0 eV [10].

In general, anatase phase is preferred in solar cells and photocatalytic applications because anatase phase has a larger band gap, potentially higher conduction band edge energy and lower electron-hole pair recombination rate [11].

Various methods have been used for preparing nanocrystalline titania thin films, such as sol-gel [12], screen-printing [13], dip-coating [14], chemical vapour deposition [15] and ultrasonic spray pyrolysis [16]. Among all these methods, ultrasonic spray pyrolysis method has been drawn considerable attention.
due to its simplicity, cost-efficiency and convenience for fabricating TiO$_2$ thin films. In this paper, TiO$_2$ thin film was deposited on the silicon and microscopy glass substrates by using ultrasonic spray pyrolysis method. The aim of this work is to deposit TiO$_2$ thin films at different substrate temperature and to investigate its structural, optical and electrical properties.

2. Experimental
TiO$_2$ thin films were deposited onto microscopy glass and c-Si substrates at different substrate temperature using ultrasonic spray pyrolysis method. The precursor solution is composed of titanium(IV) isopropoxide (TTIP) as a titanium source, acetylacetone (AcAc) as a stabilizer and ethanol as solvent. 0.2molL$^{-1}$ TTIP concentration and TTIP:AcAc molar ratio of 1:4 were used as starting solution. The solution was atomized by a ultrasonic generator of 1.7MHz frequency, produced aerosol was carried directly to the heated substrates using compressed air as carrier gas in a flow rate of 5 L/min. The deposition temperature (Ts) vary in the range 200 to 500 °C. The number of spray cycles were optimized to six.

The as-deposited films grown on glass and Si-substrates were annealed for 1 hour at 500 °C in air. The films on silicon substrates where additionally thermally treated at 700 °C for 1 hour in a laboratory furnace. The structural property of the samples was investigated by X-ray diffraction (XRD) method. XRD patterns were recorded by a Rigaku Ultima IV diffractometer with Cu K$\alpha$ radiation ($\lambda$=1.5406 Å, 40 kV at 40 mA) using Si strip detector. The measurements were performed in 2 theta/theta configurations with the scan range of 20-60 deg, with a step of 0.02 deg and a scanning speed of 2 deg min$^{-1}$. The mean crystallite size was calculated by the Scherrer method from the FWHM (full width at half maximum) of the (101) reflection of TiO$_2$ anatase phase. The surface morphology of the samples was investigated by Scanning Electron Microscopy (SEM) Zeiss HR FESEM Ultra 55 measurements with an acceleration voltage of 4.0 kV. The total transmittance of TiO$_2$ thin films is measured by Jasco V-670 spectrophotometer with a spectral range between 250 nm and 1200 nm. The film thickness was calculated by using interference fringes from the optical spectrum, and refractive index published in our previous papers [17]. Current-Voltage (I-V) measurement, taken from -1V to +1V, was performed to investigate the electrical properties of TiO$_2$ thin film on n-Si substrate. The I-V measurement was performed using graphite contact and Si as a second contact. The Autolab PGSTAT 30 system was used for measuring of I-V curves of the films.

3. Results and discussion

3.1. Morphology
The SEM images of the TiO$_2$ films deposited onto glass substrate at deposition temperatures of 200 and 500 °C and annealed at 500 °C for 1h in air are presented in Figure 1. As seen, the TiO$_2$ films are smooth, dense and free from cracks. The TiO$_2$ film deposited at 200 °C has a plane surface structure. The films deposited at 500 °C have larger well-distinguished grains with a size of ca. 50 nm.

![Figure 1. SEM surface images of TiO$_2$ thin films deposited on glass at (a) 200 °C, (b) 500 °C, and annealed at 500 °C for 1 h.](image-url)
3.2. **Structural properties**

The XRD patterns of TiO$_2$ thin films on glass substrates deposited at different deposition temperatures from 200 to 500 °C are given in Figure. 2. The diffraction peaks at 25.3, 37.7, 48.1, 53.9 and 55.1° are found to correspond to the (101), (004), (200), (105) and (211) anatase planes [18].

![Figure 2](imagepción)

**Figure 2.** XRD patterns of TiO$_2$ thin films on glass substrates deposited at various temperatures from 200 to 500 °C: (a) as-deposited thin films, (b) thin films annealed at 500 °C.

XRD studies showed that the as-deposited films prepared at substrate temperatures below 500 °C are amorphous. The anatase peak (101) becomes apparent for the films deposited at 500 °C. Annealing at 500 °C results in anatase phase for films deposited at or above 300 °C.

Figure 3 shows XRD patterns of TiO$_2$ thin films deposited on silicon substrates. XRD result showed that the films deposited at or below 300 °C are amorphous. However, the films deposited at or above 400 °C have anatase structure. Annealing at 500 °C results in the formation of anatase phase regardless of the deposition temperature. Further annealing at 700 °C has significantly changed the film structure, the films deposited below or at 400 °C remain anatase, however, the films deposited at 500 °C composed of a mixture of anatase and rutile phases.

![Figure 3](imagepción)

**Figure 3.** XRD patterns of TiO$_2$ thin films on silicon substrates. (a) as-deposited thin films, (b) thin films annealed at 500 °C, (c) thin films annealed at 700 °C.
The mean crystallite size of TiO$_2$ thin films was calculated from the (101) peak of anatase phase by the Scherrer formula. The mean crystallite size of anatase TiO$_2$ films annealed at 500 °C increased from 20 nm to 32 nm with increasing the deposition temperature from 200 to 500 °C, irrespective of the substrate.

3.3. Optical properties

The optical transmittance spectra of TiO$_2$ thin films deposited onto glass substrate at temperatures from 200 to 500 °C and followed by annealing at 500 °C are presented in Figure 4.

![Figure 4. Total transmittance spectra of TiO$_2$ thin films deposited at various temperatures: a) 200 °C, b) 300 °C, c) 400 °C, d) 500 °C on glass substrates and followed by annealing at 500 °C.](image)

The TiO$_2$ thin films were highly transparent in the visible region with total transmittance of 80 %. The total transmittance decreased with increasing the deposition temperature. The interference patterns indicate the homogeneity of the film. The decrease in the optical transmittance after annealing can be related to the increase of the light diffusion with the crystallite size and particle aggregation [19].

The optical band gap was determined using the Tauc expression [20],

$$\alpha(hv) = B(hv - E_g)^m$$

(1)

where B is a proportionality constant, hv is the photon energy, Eg is the band gap and m=2 for indirect optical transitions. The optical band gap was obtained by extrapolating the linear part of the plot of $(\alpha h v)^2$ against hv to the photon energy axis by assuming direct band gap is shown in Figure 5. The band gaps of the as-deposited films were 3.52, 3.34, 3.27, 3.25 eV, when deposited at 200, 300, 400 and 500 °C, respectively. The band gap of TiO$_2$ films decreases slightly after annealing at 500 °C and is found to be 3.51, 3.35, 3.27 and 3.12 eV, respectively. The decrease in the optical band gap of the TiO$_2$ films with annealing temperature might be the result of their increased crystallinity [21] and also their increase in the mean crystallite size.
Figure 5. The optical band gap of TiO$_2$ thin films on glass substrates: (a) as-deposited films deposited at substrate temperature from 200 to 500 °C (b) as-deposited films followed by annealing at 500 °C.

The thickness of as-deposited films increased from 110 to 620 nm with increasing deposition temperature from 200 to 500 °C. The annealing at 500 °C reduced the film thickness, remaining in the range of 80 to 500 nm, with increasing the deposition temperature from 200 to 500 °C. Since the solution feed rate was constant, then it is implicit that the film thickness increased with increasing deposition temperature owing to the corresponding increase in the reaction rate. The film thickness decreased after annealing at 500 °C, compared to as-deposited films, is related to the burning out of the organic residues in the film [22].

3.4. Electrical resistivity

Figure 6 shows the resistivity of the as-deposited and annealed TiO$_2$ films on silicon substrates. The resistivity of the films decreases with increasing deposition temperature from 200 to 300 °C, which may be due to the change of crystal structure from amorphous to crystalline anatase phase. The resistivity also decreased when increasing the annealing temperature; this phenomenon is due to an increase in the grain size which leads to a decrease in the grain boundaries and hence resistivity [23].

The equation used for the calculation of resistivity is as follows:

$$\rho = \frac{V \cdot S}{I \cdot T}$$  \hspace{1cm} (2)

Where, $\rho$ - resistivity, $\Omega$·cm; $V$-Voltage, $V$; $I$- current, $A$; $T$- TiO$_2$ film thickness, cm; $S$, the surface area of contact, cm$^2$. 

![Graph showing electrical resistivity vs deposition temperature](image-url)
4. Conclusions
Ultrasonic spray pyrolysis method was used to deposit TiO$_2$ film and the effect of deposition and annealing temperature on the structural, optical, electrical properties was investigated. The XRD data revealed that the as-deposited films grown below 400 °C onto glass substrate and below 300 °C onto Si substrate are amorphous. Annealing at 500 °C results in the formation of anatase structure, if the films are deposited at temperatures ≥ 300 °C onto glass substrates or in the temperature range 200-500 °C onto Si substrates. The mean crystallite size of anatase structure remains in the range of 20-32 nm irrespective of the deposition temperature and substrate. Further annealing of TiO$_2$ films on Si substrate at 700 °C led to the formation of the mixture of anatase and rutile phase if deposited at 500 °C and increase in the average crystallite size of the anatase structure to the range of 30-40 nm. As-deposited TiO$_2$ films show high optical transmittance and band gap values in the range of 3.52-3.25 eV if deposited at 200-500 °C. Film thickness was found to increase with deposition temperature and decrease after annealing at 500 °C. The resistivity of TiO$_2$ films depended on the deposition temperature and was found to decrease with increasing the annealing temperature.

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References
[1] Fujishima A and Honda K 1972 Nature 238 37
[2] Paul S, Choudhury A and Bojia S 2013 Micro. Nano. Lett 8 184
[3] Shin K, Yoo J B and Park J H 2013 J. Power. Sour 225 263
[4] Gong J W, Sumathy K, Qiao Q Q and Zhou Z P 2017 Renew. Sust. Energ. Rev 68 234
[5] Bai J and Zhou B X 2014 Chem. Rev 114 10131
[6] Reyes-Coronado D, Rodriguez-Gattorno G, Espinosa-Pesqueira, M E, Cab C, de Coss R and Oskam G 2018 NanoTechnology 19
[7] Nouri E, Mohammadi M R, Xu Z X, Dracopoulos V and Lianos P 2018 Phys. Chem. Chem. Phys 20 2388
[8] Lira-Cantu M, Chafiq A, Faissat J, Gonzalez-Valls I and Yu Y H 2011 Sol. Energy Mater. Sol. Cells 95 1362
[9] Mahalingam S and Edirisinghe M J 2007 Appl. Phys. A. Mater. Sci. Process 89 987
[10] Paul S and Choudhury A 2014 Appl. Nanosci 4 839
[11] Luttrell T, Halpegamage S, Tao J G, Kramer A, Sutter E and Batzill M 2014 Sci. Rep 4 4043
[12] Yu J G, Zhao X J and Zhao Q N 2000 Thin Solid Films 379 7
[13] Sauvage F, Chen D H, Comte P, Huang F Z, Heiniger L P, Cheng Y B, Caruso R A and Graetzel M 2010 ACS. Nano 4 4420
[14] Negishi N and Takeuchi K 2001 J. Solgel. Sci. Technol 2001 22 23
[15] Sun H F, Wang C Y, Pang S H, Li X P, Tao Y, Tang H J and Liu M 2008 J. Non. Cryst. Solids 354 1440
[16] Ennaceri H, Boujnah M, Taleb A, Khaldoun A, Saez-Araoz R, Ennaoui A, El Kenz A and Benyoussef A 2017 Int. J. Hydrogen. Energy 42 19467
[17] Oja I, Mere A, Krunks M, Nisumaa R, Solterbeck C H and Es-Souni M 2006 Thin. Solid. Films 515 674

Figure 6. Resistivity of TiO$_2$ films deposited on silicon substrates at various substrate temperatures (T$_s$) and after various annealing temperatures.
[18] Fazli F I M, Ahmad M K, Soon C F, Nafarizal N, Suriani A B, Mohamed A, Mamat M H, Malek M F, Shimomura M and Murakami K 2017 Optik 140 1063
[19] Ben Karoui M, Kaddachi Z and Gharbi R 2015 Proc. Tunisia-Japan Symposium - R&D of Energy and Material Sciences for Sustainable Society (Gammarth, 2014) 596
[20] Tauc J 1968 Mater Res Bull 3 37
[21] Lin C P, Chen H, Nakaruk A, Koshy P and Sorrell C C 2013 Proc. 10th Eco-Energy and Materials Science and Engineering Symposium (Ubon Ratchathani, 2012) 34 627
[22] Oja I, Mere A, Krunks M, Solterbeck CH and Es-Souni M 2004 Proc. Symposium on Functional Nanomaterials for Optoelectronics and other Applications (Warsaw, 2003) 99 259
[23] Bakri A S, Sandan M Z, Adriyanto F, Raship N A, Said N D M, Abdullah S A and Rahim M S 2017 Proc. Int. Conf. on Engineering, Science and Nanotechnology (Solo, 2016) 1788