

Influence of Ag-doping on The Optical and Structural properties of TiO₂ Thin Films Deposited by Electrohydrodynamic Spray Pyrolysis.

ABSTRACT

Aims: To study of the structural and optical properties of undoped titanium (IV) oxide (TiO₂), 1.0 M of silver-doped TiO₂ and 1.5 M silver-doped TiO₂.

Study Design: Electro- hydrodynamic spray pyrolysis technique was used in the study.

Place and Duration of Study: titanium acetyl acetate [Ti(C₅H₇O₂)₄] , propanol [C₃H₈O] and silver nitrate [AgNO₃] was obtained from Sheda Science and Technology Complex (SHESTCO) Abuja (Nigeria). The study was carried out between March 2017 and November 2017 at Sheda Science and Technology Complex (SHESTCO) Abuja (Nigeria).

Methodology: TiO₂ was synthesized using 0.2 mol of titanium acetyl acetate [Ti(C₅H₇O₂)₄] and 20 mol of propanol [C₃H₈O] as the precursor. The silver (Ag) was obtained using 0.68 g of silver nitrate [AgNO₃], mixed with 20 mol of propanol in a conical flask and placed on a magnetic stirrer. The flow rate by volume was set at 4200 microlitres/hour and the time of deposition was set at 10 mins. The Electrohydrodynamic Spray Pyrolysis Technique was set at voltage of 3.5 KV and the distance between the nozzle and the substrate (pro cleaned glass) was 5.95 mm. (1.0 and 1.5)M of silver (Ag) doped TiO₂ was deposited at 250°C. Undoped TiO₂ was also deposited at 250°C.

Results: The films were characterized by Surface Profilometry, Ultraviolet – Visible light Spectroscopy (UV-Vis Spectroscopy) and X-ray diffraction (XRD). The results from surface profilometry showed that all the samples were thin films. XRD results reviewed crystalline structure of TiO₂. The crystal phase observed for both TiO₂ and silver-doped TiO₂ is “trigonal”. The results of (UV-Vis Spectroscopy) shows that the undoped TiO₂ exhibited low absorbance within the visible spectrum but increased as we dope with 1.0 M and 1.5 M Ag-doped TiO₂ added respectively. The results also showed that all the films have high transmittance around 50- 97% in the visible region and NIR of the spectrum such that we can use them as optical windows in solar cells. Extinction coefficient increases within the visible region as we doped and the results also showed that the absorption coefficient, the direct transition and indirect transition can be controlled. The direct band-gap for the films range from 3.81 eV- 3.00 eV while the indirect band-gap for the films range from 3.80 eV – 2.6 0eV. The energy gap is decreased gradually whenever the impurities rate increases.

Keywords: Ag doped TiO₂, Spray Pyrolysis, Structural Properties, Optical Properties, Heterogeneous Photocatalysis

INTRODUCTION

Transparent metal oxides (TMOs) in most cases have served as the inorganic semiconducting component. Among the materials reviewed titanium (IV) oxide, TiO_2 is the most promising electron acceptor because it offers good electron transport [1], excellent physical and chemical stability [2]. It is one of the most important nanomaterials which have attracted a great attention due to its unique characteristics such as low cost, easy handling, non-toxicity, and resistance to photochemical and chemical erosion [3]. Due to a combination of such unique properties as high refractive index, high transmittance, chemical stability and photo-catalytic behaviour, titanium dioxide constitutes a very valuable material for optical applications [4]. Recently, scientific efforts have been drifted toward's shifting the optical sensitivity of the TiO_2 from UV to the visible-light spectrum for the efficient use of solar radiation or artificial visible light [5]. It is generally accepted that the presence of metal or non metal dopants into TiO_2 lattice increases the photocatalytic activity of the mater under visible light irradiation [6]. However, producing porous TiO_2 samples with large surface area can improve its photocatalytic properties by means of reducing the recombination rate of photo induced electron-hole pairs. This is due to their faster arrival to the reaction site of the surface and efficient charge separation which increases the lifetime of the charge carriers and enhances the photocatalytic efficiency [7]. The aim of this work is to produce high-quality silver (Ag)-doped TiO_2 thin films for optical application by using Electro-hydrodynamic Spray Pyrolysis Method. Distinctive attention was paid to the influence of the processing factors, such as dopant concentration into the targets on the optical properties of the films during the deposition.

EXPERIMENTAL

TiO₂ was synthesized using 0.2 mol of titanium acetyl acetate [Ti(C₅H₇O₂)₄] and 20 mol of propanol [C₃H₈O] as the precursor. The silver (Ag) was obtained using 0.68 g of silver nitrate [AgNO₃], mixed with 20 mol of propanol in a conical flask and placed on a magnetic stirrer. The flow rate by volume was set at 4200 microlitres/hour and the time of deposition was set at 10 mins. The Electro-hydrodynamic Spray Pyrolysis Technique was set at voltage of 3.5 KV and the distance between the nozzle and the substrate (pre-cleaned glass) was 5.95 mm. From the precursors we obtained



(1.0 and 1.5)M of silver (Ag) doped TiO₂ was deposited at 250°C. Undoped TiO₂ was also deposited at 250°C. The thicknesses of the synthesized samples (both doped and undoped) were measured using surface profilometry with a VeecoDektak 150 profiler machine. Using UV-Vis spectroscopy, the absorption spectra, extinction coefficient, absorption coefficient, refractive index of the deposited undoped TiO₂ and Ag-doped TiO₂ thin films were also recorded. Using the law of conservation of energy [8] the reflectance values of the samples were obtained. Where (A) absorbance, (T) transmittance and (R) reflectance respectively.

$$A + T + R = 1 \quad (2)$$

From equation 2, reflectance (R) was given as

$$R = 1 - T - A \quad (3)$$

The optical constants are the index of refraction (η) and the extinction coefficient (k). The optical constants of a thin film material are most commonly and reliably determined from the simultaneous measurement of transmittance and reflectance of the film. The values of the refractive index of the samples were obtained using (equation 4) [8].

$$\eta = (1 + \sqrt{R}) / (1 - \sqrt{R}) \quad (4)$$

Where R is the reflectance and η is the refractive index.

Absorption Coefficient measures the rate of decrease in the intensity of electromagnetic radiation (beams of photons or particles), as it passes through a given substance. The absorption coefficient determines how far into a material light of a particular wavelength can penetrate before it is absorbed. The results of the absorption coefficient of the samples were obtained using (equation 5) [8].

$$\alpha = \ln \left[\frac{1}{T} \right] / d \text{ eVm}^{-1} \quad (5)$$

Where, T is the transmittance, d is the thickness and α is the absorption coefficient.

The values of extinction coefficient of the samples were calculated using (equation 6) [9].

$$K = \alpha \lambda / 4\pi \quad (6)$$

Where k is called the extinction coefficient (k), α is the absorption coefficient, λ is the wavelength.

The X-ray diffraction pattern was recorded on a RigakuUltima IV X-ray diffractometer equipped with a graphite-monochromated Cu K α radiation source (40 kV, 30 mA) and wavelength 1.54 Å. A diffractogram was collected in the 2 θ range between 3° and 90° with a step size of 0.01° and a scan speed of 1°/min. the XRD Pattern was processed using JCPDS card numbers. We used Debye Scherer Equation to determine the crystallite size.

$$D = k\lambda / \beta \cos\theta \quad (7)$$

Where D is the crystallite size, K= shape factor, which is constant (0.89), λ = wavelength (1.54Å), β = Full Width Half Maximum (FWHM), θ = 2 Theta.

The Tauc's relation (Equation 8) was used to estimate the optical band gap

$$\alpha h\nu = A(h\nu - E_g)^n \quad (8)$$

Where $h\nu$ is the photon energy, h is Planck's constant, α is the absorption Coefficient, A is the constant, for direct transitions $n=2$, and E_g is the optical band gap, which is given as

$$E_g = h\nu = \frac{hc}{\lambda} \quad (9)$$

Where C is the velocity of light, λ is the wavelength in meters (m), ν is the transition frequency and h is the Planck's constant. Since $1\text{J} = 1.602 \times 10^{-19} \text{ eV}$ We substituted these variables into equation 9 and obtained

$$h\nu \text{ (eV)} = \frac{1.241}{\lambda(\mu\text{m})} \quad (10)$$

From equation 10 we calculated the photon energies in (eV) for various wavelengths λ in(μm). A graph of $(\alpha h\nu)^2$ versus $h\nu$ for both undoped and doped samples were plotted and the direct band gap was determined by extrapolating the straight portion of the graph on $h\nu$ axis at $(\alpha h\nu)^2 = 0$ which gives the band gap of both doped and undoped films. Figure 6 shows the plot of $(\alpha h\nu)^2$ against photon energy. The direct band gap energy was extrapolated at the axis of the photon energy ($h\nu$) where $(\alpha h\nu)^2 = 0$. The Figure gives the direct band gap of 3.81eV for undoped or pure TiO_2 , 3.20 eV for 1.0 M of Ag/TiO_2 and 3.00 eV for 1.5 M of Ag/TiO_2 . The direct band gap of undoped or pure TiO_2 3.81eV is in agreement with the result of undoped TiO_2 obtained by [10]. From the results, these band gap values shows that optical band gap energies of pure or undoped TiO_2 decreases with doping of silver ions, which allow the delay in the recombination rate and enhances the photocatalytic activities of TiO_2 [11].

RESULTS AND DISCUSSION

The thickness of the synthesized samples (both doped and undoped) was measured using surface profilometry with a VeecoDektak 150 profiler machine; the result showed that all the samples are thin films.

The absorbance spectra of the deposited films were shown in Figure 1. It is obvious that the absorption edge was shifted to visible region due to Ag doping. Hence, silver (Ag) doping caused decrease in the energy band-gap of the films. The more we dope with Ag, the higher the absorbance within the visible region. This result is agreement with results obtained by [12] and [10] .

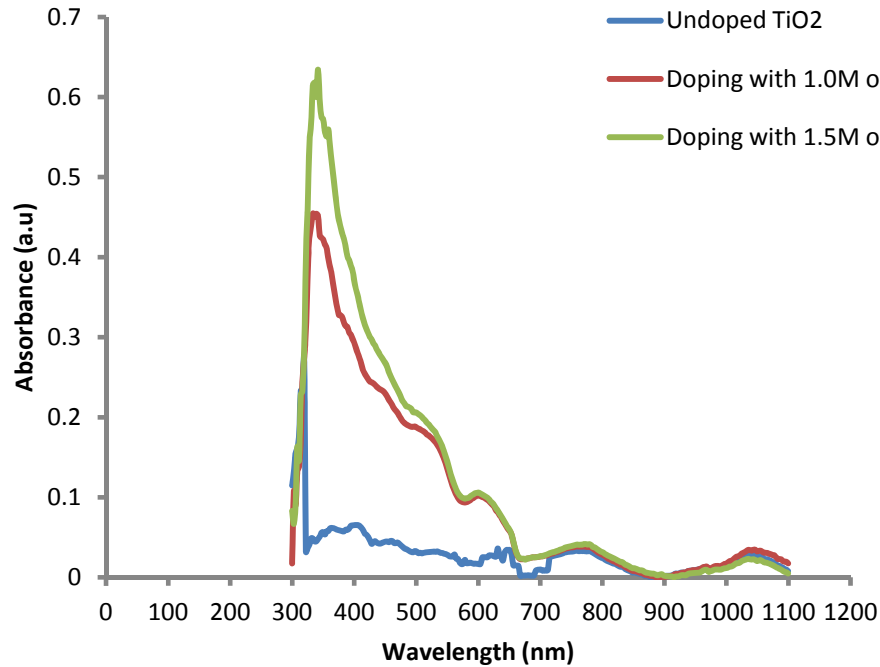


Figure 1: Absorbance Spectra for the Undoped and Doped Samples.

From the result obtained in Figure 2, we observed that the average transmittance of all the deposited films is above 75% in the visible region which is in agreement with the result obtained by Hassan *et al.*, [13]. We also observed that the effect of doping with different concentrations of silver brought about slight decrease in the transmittance within the visible region which is also in agreement with results obtained from [14].

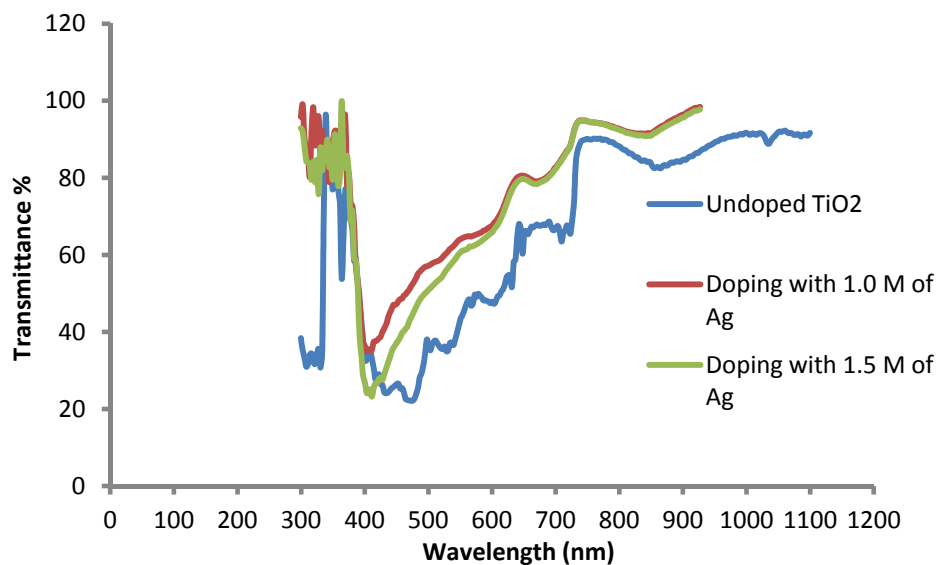


Figure 2: Dependence of Transmittance on Wavelength for Undoped and Doped Samples.

The result obtained in Figure 3 shows that absorption coefficient is inversely proportional to the transmittance. Increase in Ag content increased the absorption coefficient of the films within the visible region. The result is accordance with result obtained by [15].

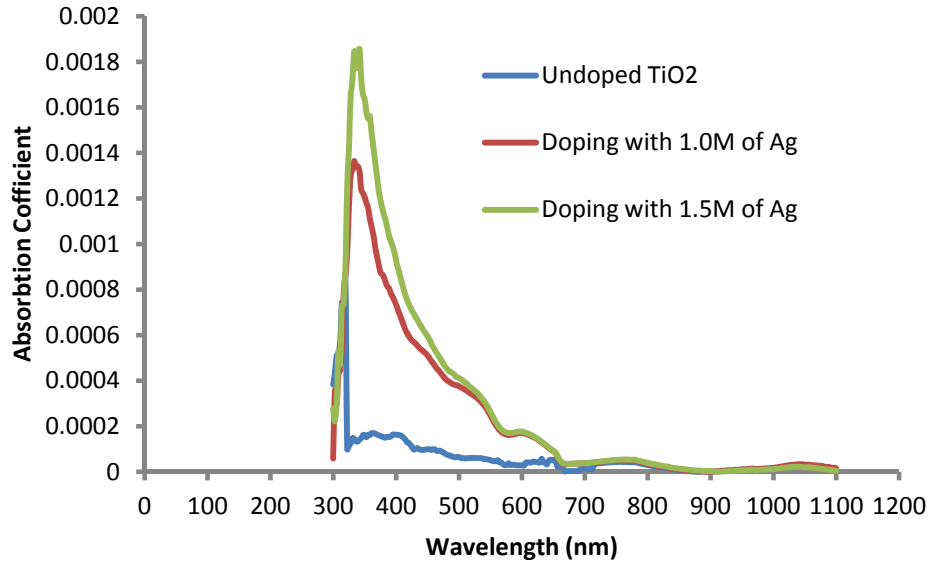


Figure 3: Absorption Coefficient against Wavelength for Undoped and Doped Samples

Figure 4 shows the variation in refractive index films with wavelength. It is observed that the refractive index for the films have sharp increase in the wavelength of 390nm to 400nm and then the curve increased slowly with further increase in the wavelength.

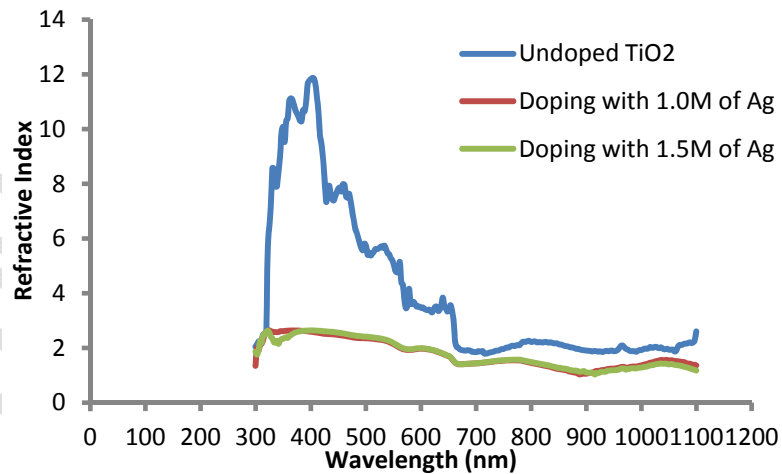


Figure 4: Variation of Refractive index for Undoped and doped Samples.

Fig. 5 shows the variation in extinction coefficient of the films deposited. It is clear that the graph of the extinction coefficient has the same behaviour with that of the absorption (absorbance). The influence of doping TiO_2 with different concentration of Ag brought about increase in the Extinction coefficient due to increase in the absorption. Hence as the concentration of Ag increased, the Extinction Coefficient increased. This result is in agreement with the result obtained by [10].

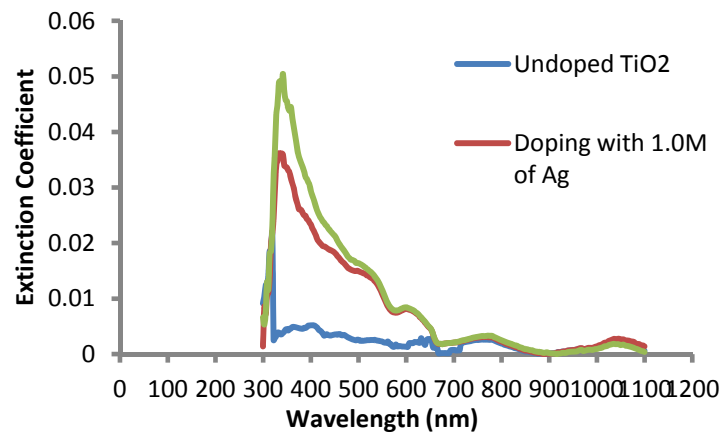


Figure 5: Dependence of Extinction Coefficient on the Wavelength for Undoped and Doped Samples.

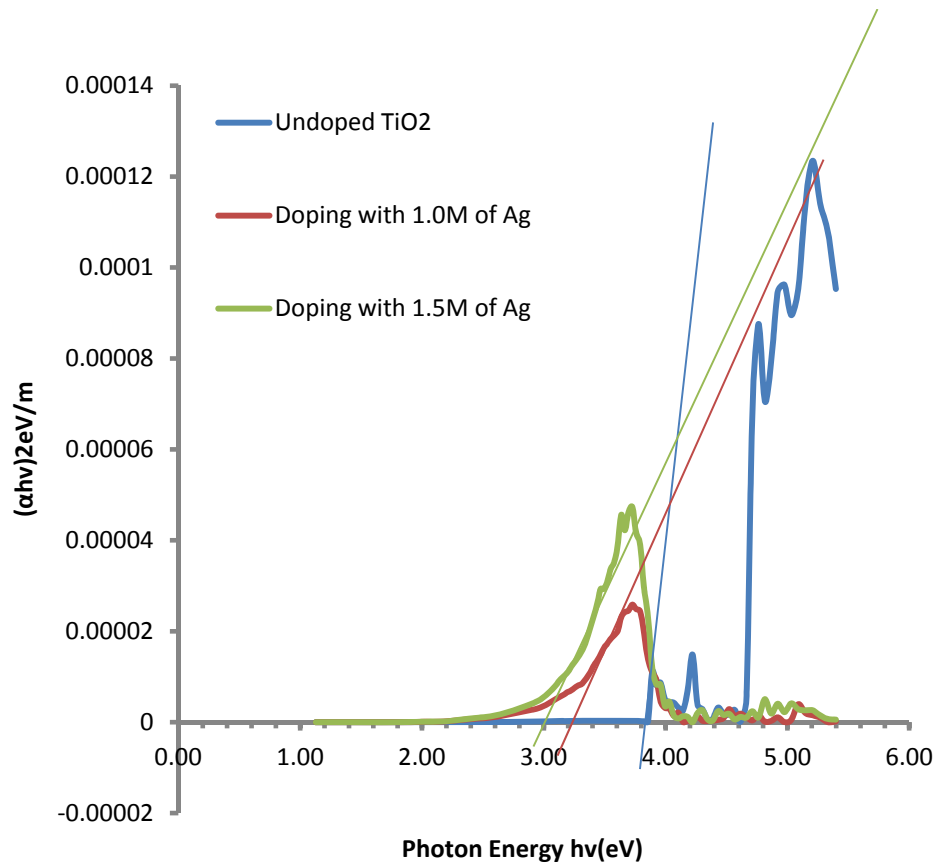


Fig 6: Direct Band gap for Undoped and Doped Samples.

Figure 7 shows the plot of $(\alpha h\nu)^{1/2}$ against photon energy. The indirect band gap energy was also extrapolated at the axis of the photon energy ($h\nu$) where $(\alpha h\nu)^{1/2} = 0$. Figure 6 gives the indirect band gap of 3.80 eV for undoped TiO_2 , 2.80 eV for 1.0 M of Ag/TiO_2 and 2.60 eV for 1.5 M of Ag/TiO_2 . From the results, these band gap values shows that optical band gap energies of pure or undoped TiO_2 decreases with doping of silver ions, which allow the delay in the recombination rate and enhances the photocatalytic activities of TiO_2 [11].

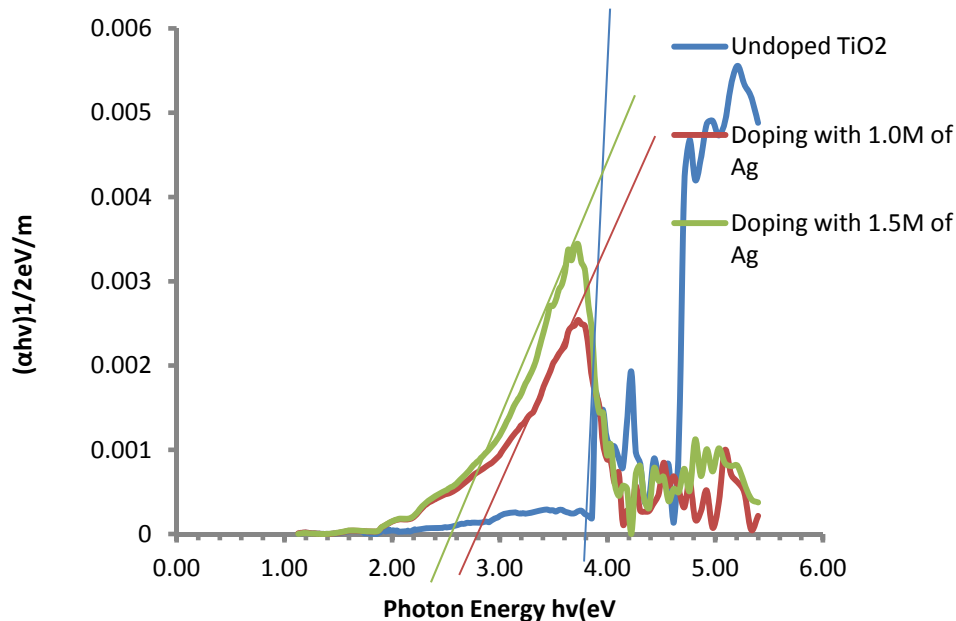
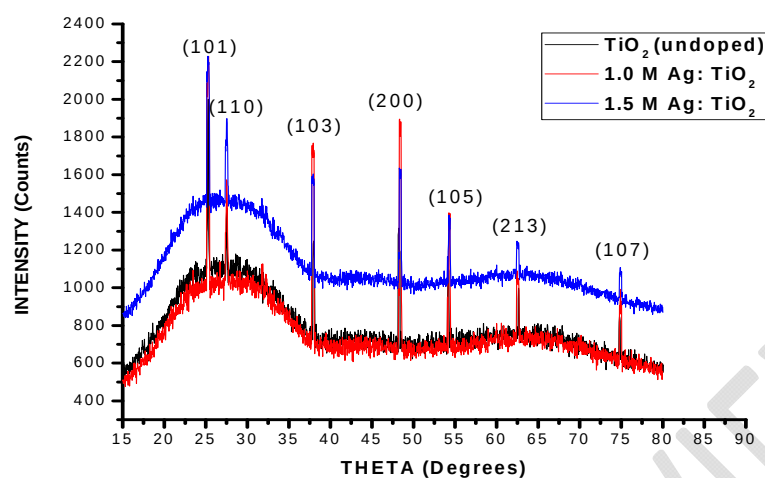


Fig 7: Indirect Band gap for Undoped and Doped Samples.

The X-ray Diffraction

The X-ray diffraction patterns for both undoped TiO_2 and doped samples with peaks at $2\theta = 25.30^\circ, 27.56^\circ, 37.99^\circ, 48.25^\circ, 54.22^\circ, 62.65^\circ$ and 74.80° which correspond to miller indices $[101], [110], [103], [200], [105], [213]$ and $[107]$, respectively. These results correspond to crystalline phase of TiO_2 . Using Debye-Scherrer equation, $D = k\lambda / \beta \cos\theta$ the average crystallite was 8.76nm, 8.90nm and 9.00nm respectively. Comparing the three patterns we observed that increase in the impurities (concentration of Ag) brings about increase in the intensity of the peaks hence increasing the crystallinity of the films.



CONCLUSION

In this paper we have reported the structural, optical properties of TiO₂ and Ag-doped TiO₂ synthesized using Electro hydrodynamic spray pyrolysis equipment. The X- ray diffraction pattern showed crystalline nature of TiO₂. The UV- vis spectroscopy revealed the shifting of absorption edge of silver-doped TiO₂ to the visible region compared to that of Undoped TiO₂. The Extinction coefficient showed that as the dopants are been added to the parent material, the extinction coefficient values of the films increases within the visible region. The average transmittance for TiO₂ films is over 75% hence we can use these samples as an optical window in solar cell. Also the optical properties of the thin films have allowed direct transition and allowed indirect transition. Increase of the Ag content of the films causes a decrease in the optical band gap values, hence the undoped TiO₂ film showed poor photocatalytic activity, while doping of silver ions improves the efficiency under the visible –light radiation.

1. Nowotny, J., Radecka, M., Rekas, M., Sugihara, S., Vance, E.R., and Weppner, W. Electronic and ionic Conductivity of TiO_2 single Crystal within the n-p Transition Range. *International Journal of Ceramics*. 1998: 24, 571- 577.
2. Fujishima, A., and Zhang, X. Titanium Dioxide Photocatalysis: Present Situation and future Approaches. *Journal of Kanagawa Academy of Science and Technology*. 2006: 9, 750-760.
3. Hoffmann, M. R., Martin, S.T., Choi, W., and Bahnemann, D. Environmental Applications of Semiconductor Photocatalysis. *Journal of Chemical reviews*. 1995: 95, 69-96.
4. Lien, S., Wu, D., Yeh, W., and Liu, J. Tri-layer antireflection coatings ($\text{SiO}_2/\text{SiO}_2\text{-TiO}_2/\text{TiO}_2$) for silicon solar cells using a sol-gel technique, *Solar Energy Materials & Solar Cells*. 2006: 90, 2710-2719.
5. Janitabar-Darzi, S., Mahjoub, A.R., and Bayat, A. Synthesis and Characterization of visible light active S-doped TiO_2 Nanophotocatalyst. *International Journal of NanoDimens*. 2016: 7, 33-40.
6. Asiri, A. M., Al-Amoudi, M. S., Bazaid, S. A., Adam, A. A., Alamry, K. A., and Anandan, S. Enhanced visible light photodegradation of water pollutants over N-, S-doped titanium dioxide and n-titanium dioxide in the presence of inorganic anions. *Journal of Saudi Chemical Society*. 2014: 18, 155-163.
7. Janitabar-Darzi, S., Mahjoub, A. R., and Nilchi, A. Investigation of structural, optical and photocatalytic properties of mesoporous TiO_2 thin film synthesized by Sol.Gel templating technique *Journal of Physica E*. 2009: 42, 176.181.
8. Ali, M.S., Farooq, W.A., Baig, M.A., Shar, M.A., Atif, A.S.S., Alghamdi, M.S., and Aziz, M. H. (2015). Structural and Optical Properties of Pure and Ag doped ZnO Thin Films obtained by Sol-gel Spin Coating Technique. *Journal of Materials Science-Poland*. 2015: 33, 601-608. <http://dx.doi:10.1515/msp-0091>.
9. Mahrov, B., Boschloo G., Hyfeldt A., Siegbahn H., and Rensmo H. Photoelectron Spectroscopy Studies of $\text{Ru}(\text{dcbpyH}_2)_2(\text{NCS})_2/\text{CuI}$ and $\text{Ru}(\text{dcbpyH}_2)_2/\text{CuSCN}$ Interfaces for Solar Cell Applications. *Journal of Physical Chemistry*. 2004: 108, 11604–11610.
10. Yousif, A.A., Aadim, A. K., and Hamzah, A. N. Influence of Ag doping on Optical Properties of Nanocrystalline Titanium Dioxide prepared by PLD. *Journal of Applied Physics (IOSR-JAP)*. 2016: 8, 50-56.
11. Gupta, K., Singh, R.P., Pandey, A., Pandey A., and Beilstein, J. Photocatalytic Antibacterial Performance of TiO_2 and Ag-doped TiO_2 against *S. aureus*, *P. aeruginosa* and *E. coli*. *Journal of Nanotechnology*. 2013: 4, 345–351. <http://dx.doi:10.3762/bjnano.4.40>.
12. Behnajady, M.A., Modirshahla, N., Shokri, M., and Rad, B. Enhancement of Photocatalytic Activity of TiO_2 Nanoparticles by Silver doping: Photodeposition versus Liquid Impregnation Methods. *Journal of Physical Chemistry*. 2007: 35, 10173-10182.
13. Hassan, M.M., Haseeb, A.S., Saidur, H., and Masjuki, M. Effects of Annealing Treatment on Optical properties of Anatase TiO_2 Thin films. *International Journal of Chemical and Biomolecular Engineering*. 2008: 1, 93-97.

- 244 14. Firdaus, C.M., Rizam, M.S.B., Rusop, M., and Hidayah, S.R. Characterization of ZnO and ZnO: TiO₂
245 Thin Films Prepared by Sol-Gel Spray-Spin Coating Technique. International Symposium on
246 Robotics and Intelligent Sensors. 2012: 41, 1367-1373.
- 247 15. Ichinose, I., He, J., Kunitake, T., and Nakao, A. In situ Synthesis of Nobel metal Nanoparticles
248 in ultrathin TiO₂ – gel films by a combination of ion-exchange and reduction processes. Journal
249 of Langmuir. 2002: 18 , 10005-10010.