Sol gel spin coated TiO_2 films for transparent window applications

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TiO_2 films of different thickness were deposited using Sol-Gel spin coating technique using titanium isopropoxide [Ti $(OC_3H_7)_4$] as a precursor. The films were characterized using X-ray diffraction, scanning electron microscopy (SEM) and UV-Vis spectroscopy. The XRD spectra indicate the presence of brookite TiO_2 phase in the films. The grain size as calculated using the Scherrer's formula was found to be 28.7, 37.8 and 47.9 nm for TiO_2 (121) film of thickness 100, 200 and 300 nm respectively. The grain size increases with increase in thickness of the films. The SEM micrographs show uniformly distributed grains which appear to grow with the thickness. The optical band gap of the TiO_2 films of different thickness show a change from 3.55eV to 3.35 eV. The extinction coefficient of the films appears to lie in the range 0.021-0.29.

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1. Introduction

Transparent conductors in the form of transparent conducting oxides (TCOs) are critical components in many optoelectronic applications including flat panel displays (FPD) and photovoltaics as well as organic electronics including both organic light-emitting diodes (OLED) and organic photovoltaics (OPV) [1,2]. Unlike most metals which are opaque and most transparent materials, which are insulating, TCOs are a special class of wide band gap (~ 3eV) metal oxide semiconductors such as ZnO, SnO_2 and In_2O_3, which can support high enough free electron concentrations to be effective electrical conductors [3]. TCOs are generally based on a limited class of metal oxide semiconductors such In_2O_3, ZnO and SnO_2, which are transparent due to their large band gap energy and can also tolerate very high electronic doping concentrations to yield high conductivity. However, these three basic TCOs alone do not meet the TCO performance needs of emerging PV and other applications. Another TCO like TiO_2 has also been synthesized by techniques like thermal oxidations, sputtering and electron gun etc. [4-7]. Over the years titanium oxide is one of the extensively studied transition metal oxides. Titanium dioxide is chemically stable, relatively hard, non-toxic, bio-compatible, largely transparent and inexpensive. Its particularities are a high dielectric constant and an interesting photocatalytic activity. It is a wide gap semiconductor with a large range of electrical conductivity depending on its chemical composition. Titanium dioxide possesses three different crystal structures: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Among these brookite phase is very rarely observed, rutile is most stable phase whereas anatase is the metastable phase. For TCOs, scaling up the low cost techniques for industrial application is still is big challenge. Spin coating is a low cost technique and provide the possibility of scale up the coating process for large area substrates for industrial applications. It involves the acceleration of a liquid puddle on a rotating substrate. The spin coating material is deposited in the centre of the substrate either manually or by robotic arms. The physics behind the spin coating involves a balance between centrifugal forces controlled by spin speed and viscous forces which are determined by solvent viscosity. Keeping these points in view, spin coating technique has been exploited for preparing TiO_2 films. The structural and optical properties of TiO_2 films as a function of thickness are presented in this communication.

2. Experimental

The sol-gel method has been employed to prepare TiO_2 solution. The 0.5M TiO_2 solution was prepared by dissolving the titanium alkoxide precursor i.e. titanium isopropoxide (Ti $(OC_3H_7)_4$) in an alcoholic bath. To avoid the early precipitation of the oxides 5 ml of concentrated HCl was used per 100 ml of the ethyl alcohol. After addition of the concentrated HCl, solution was stirred vigorously up to 1h till the gel formation. The films has been prepared on the glass substrate by the spin coating technique using MILMAN spin coating unit (MODEL 2000S). The thickness of the films was analyzed by DEKTEK profilometer and was found to be nearly 100,200 and 300 nm. The structural analysis of the films under investigation was done using Scanning Electron Microscope (SEM) and X-ray diffraction (XRD). The JOEL JSM-6100 (Japan) scanning microscope and Philips diffractometer were used for these purposes respectively. For SEM studies films deposited on glass substrate were coated with thin (100Å) gold films before micrographs

could be recorded. X-ray diffractogram has been recorded in the range 10^o-90^o (2θ) at a scanning speed of 1^0 per minute. All structural measurements were taken at room temperature. To study the optical properties, the absorbance spectra of the samples were obtained at room temperature in the wavelength ranging from 200nm to 1100nm by using UV-160A (Shimadzu) spectrophotometer.

3. Results and discussion

3.1 Structural analysis

Fig 1 (a) shows the X-ray diffraction pattern of TiO_2 film of thickness 100 nm. Two prominent peaks corresponding to d-values 3.51 Å and 2.87 Å have been observed. The corresponding indices are (120) and (121), which confirms the presence of brookite phase. Similar observations are reported by Jalava et. al. [8] for TiO_2 films prepared thermal hydrolysis techniques. The X-ray diffraction pattern of TiO_2 films of thickness 200 nm and 300 nm are shown in fig 1(b) and fig 1(c) respectively. These films show comparatively intense peak corresponding to d value 2.87 Å, while diffraction peak with d value 3.51 Å has been disappeared. These observations confirm the growth of single phase (brookite) TiO_2 films. Also the decrease in full width half maxima (FWHM) of diffraction peak with d value 2.87Å has been noticed, thus suggesting a high degree of crystallinity with increase in thickness.

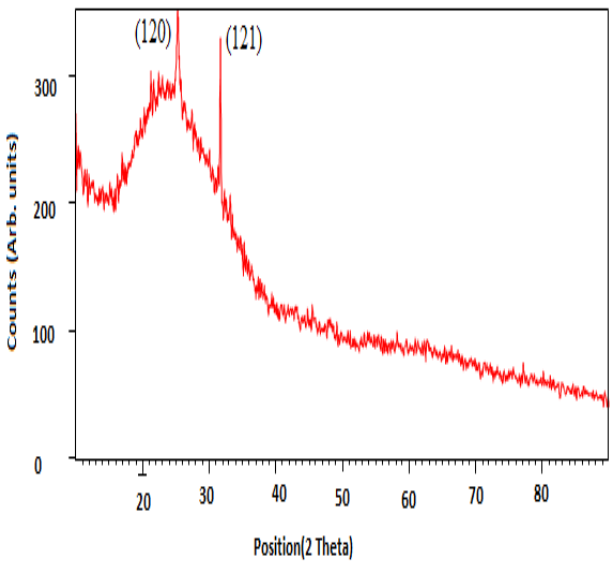

Fig 1(a) :- X-ray diffraction pattern of TiO_2 film of thickness 100nm.

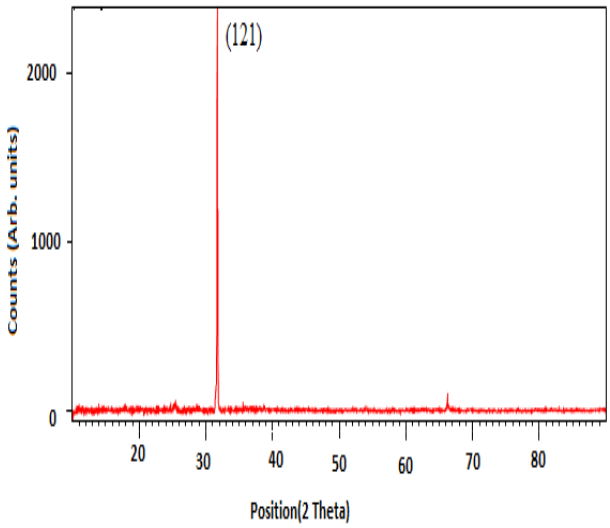

Fig 1b:-X-ray diffraction pattern of TiO_2 film of thickness 200 nm.

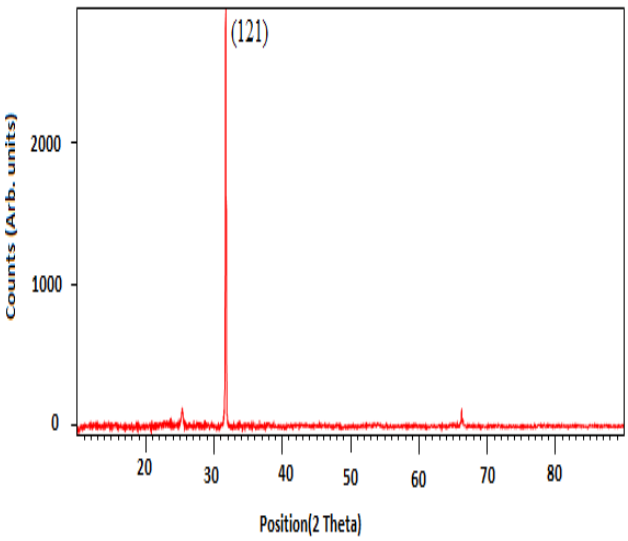

Fig 1c:-X-ray diffraction pattern of TiO_2 film of thickness 300nm.

The average particle size (Table 1) is calculated from FWHM of XRD pattern of films by using Scherrer's formula[9]

$$D=k\lambda/ß\cos\theta \quad (1)$$

where D is the particle size, k is the shape factor, λ is the x-ray wavelength typically 1.54 Å, ß is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. Observation reveals that particle size increases with increase in thickness of the films (Table 1). Similar results are also reported by Jiaguo Yu et. at. [10] for TiO_2 films of different thickness.

Table 1: Particle size obtained for TiO_2 films of different thickness.

Thickness (nm)	(hkl) planes	d (inter planer spacing)Å	2θ	FWHM(ß)	Particle size (D) in nm
100	(121)	2.87	31.06	0.005	28.7
200	(121)	2.87	31.06	0.0038	37.8
300	(121)	2.87	31.06	0.003	47.9

3.2 Scanning Electron Microscopy

SEM has been used as an essential tool to analyze the dependence of the film texture on growth parameters. SEM micrographs illustrate the distribution, shape and size of crystallites. The SEM micrographs of 100nm, 200nm and 300nm TiO_2 thick films are shown in figures 2 (a-c) respectively. These micrographs show the formation of well defined crystallites with remarkable separation from each other. The formation of separated crystallites is probably due to the low concentration of the Ti [11]. On average the dimensions of the crystallites are found to be 5µm long and 4µm wide for 100nm thick film.

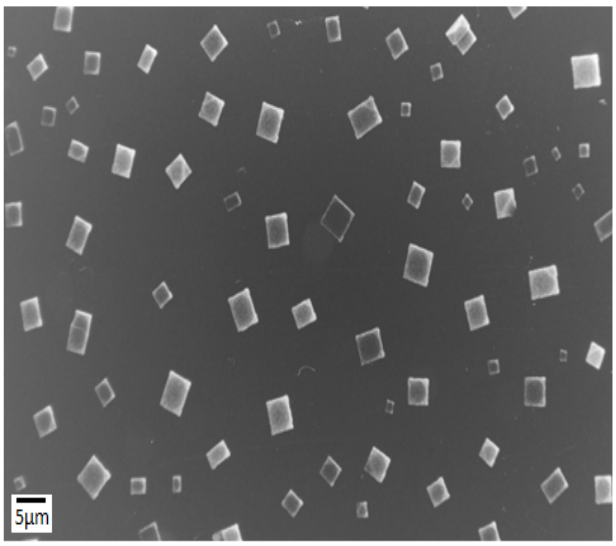

Fig 2a:-SEM image of TiO_2 film of thickness 100nm.

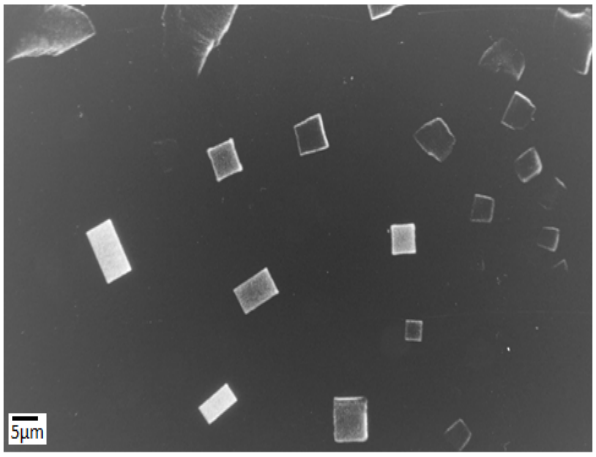

Fig 2b:- SEM image of TiO_2 film of thickness 200nm.

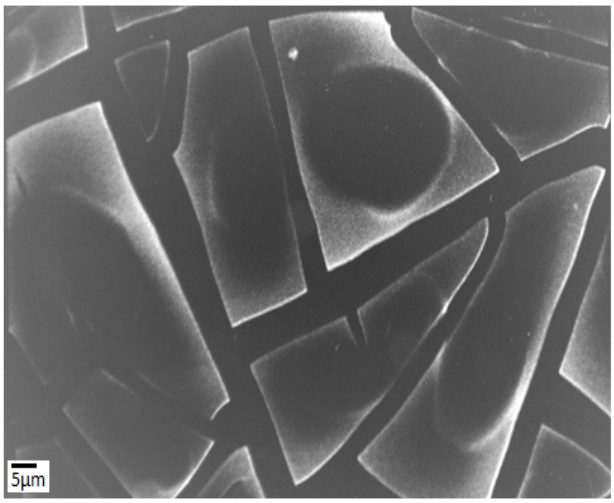

Fig 2c:- SEM image of TiO_2 film of thickness 300nm.

It is important to mention here that with increase in thickness, the dimensions of the crystallites increases. Thus crystallinity of the films increases with increase in thickness of the films. This may be attributed to the fact that initial layers act as a nucleation centre for further growth of crystallite.

4 Optical Characterizations

4.1 UV-VIS Spectroscopy

Figs. 3 (a-c) shows the UV-VIS absorption spectra of films with different thickness deposited onto glass substrate by spin coating technique. It is observed from the absorption spectra of the films that an absorption hump occurs at wavelength 320 nm and absorbance increases with increase in thickness of the films. It is also important to note here that with increase in thickness, the absorption spectrum show broadening, covering wide range of absorption spectrum.

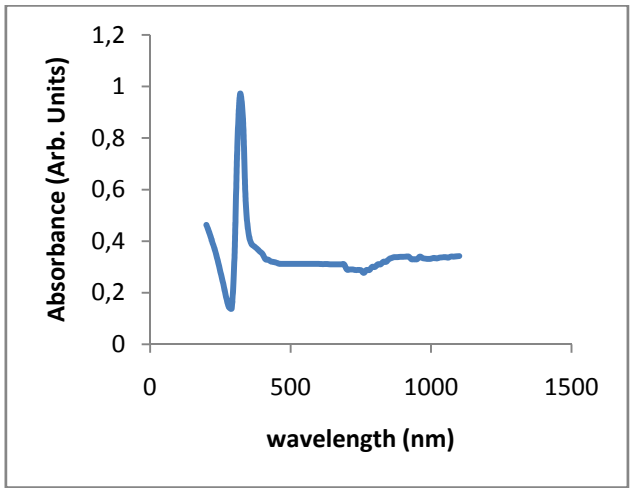

Fig 3a:-UV-VIS absorption spectra of TiO_2 film of thickness 100nm

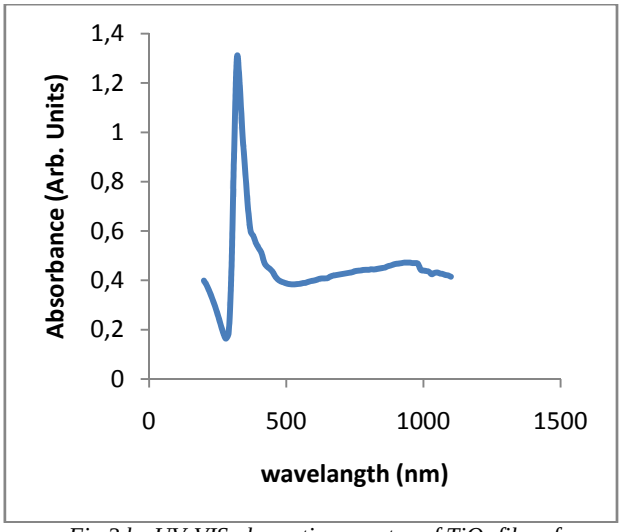

Fig 3 b:-UV-VIS absorption spectra of TiO_2 film of thickness 200nm.

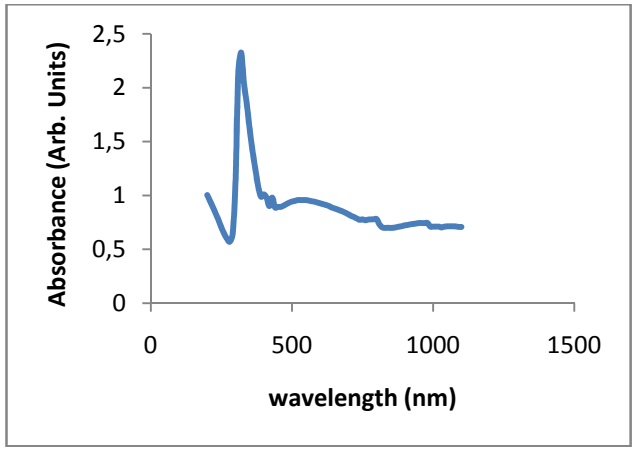

Fig 3c:-UV-VIS absorption spectra of TiO_2 film of thickness 300nm.

The absorption coefficient of TiO_2 films of different thickness deposited onto the glass substrate has been determined over the range 1.15-3.75 eV, which show an absorption edge in the lower energy region of the spectra of the films taken over 200-1100 nm range. The absorption edge of the TiO_2 films have been examined in terms of a direct transition using the equation of Bardeen et. al. [12] stating that

$$\alpha h\nu = B(h\nu - E_g)^n \quad (2)$$

where n=1/2 for direct allowed transitions. As observed from figures 4(a-c), the spectral variation of absorption coefficient, in the range 1.15-3.75 eV appear to follow the relation

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \quad (3)$$

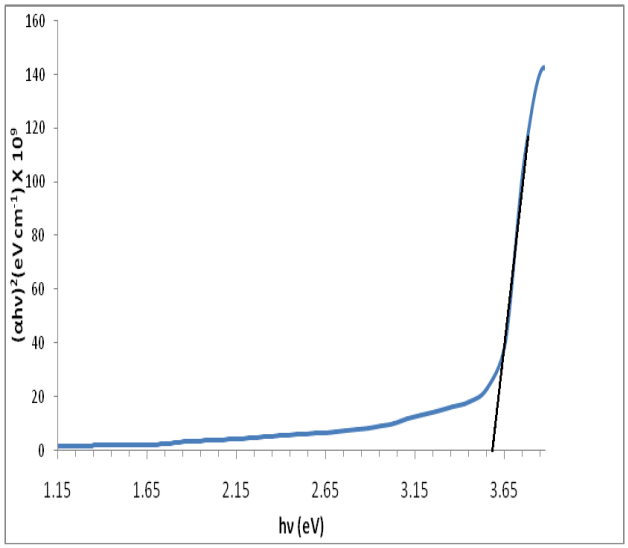

Fig 4 a:-Variation of optical absorption coefficient with photon energy (1.15-3.75 eV) under direct transition for TiO_2 film of thickness 100 nm deposited onto glass substrate.

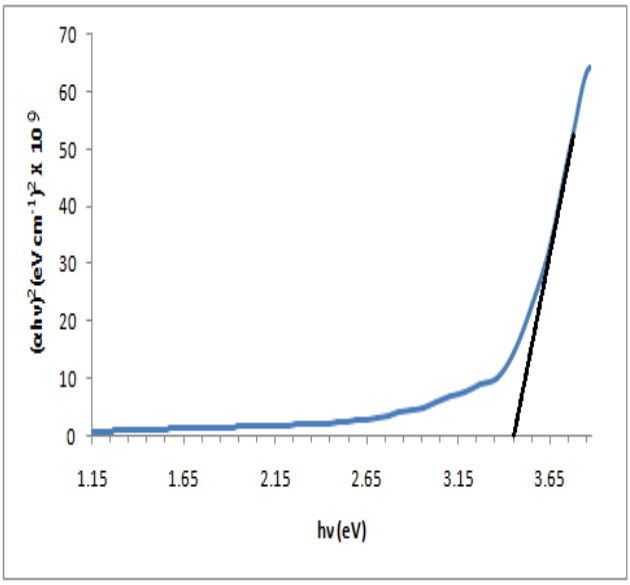

Fig 4b:-Variation of optical absorption coefficient with photon energy (1.15-3.75 eV) under direct transition for TiO_2 film of thickness 200 nm deposited onto glass substrate.

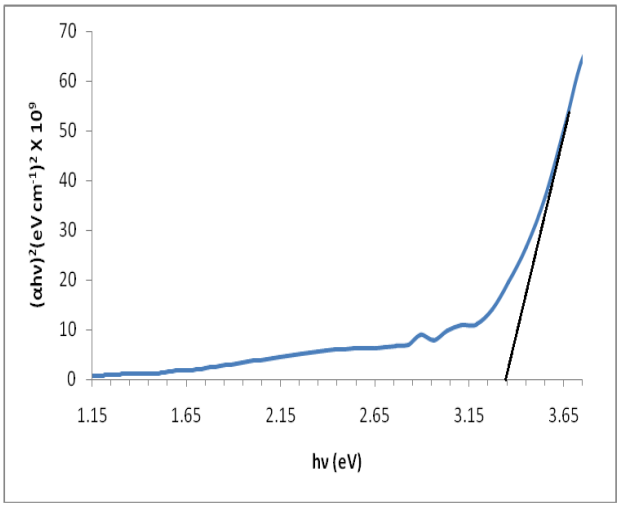

Fig 4c:-Variation of optical absorption coefficient with photon energy (1.15-3.75 eV) under direct transition for TiO_2 film of thickness 300 nm deposited onto glass substrate.

The extrapolation of the linear portion to αhν=0 gives the value of the optical band gap under direct allowed transitions. It has been observed that the optical band gap energy decreases with increase in thickness and found to be lie in the range 3.55- 3.35 eV. However, Chen Y. et. al. [13] has estimated the band gap of electron beam evaporated TiO_2 films deposited onto glass substrate kept at different substrate temperature to be lie in the range 3.81 to 3.92 eV.

The extinction coefficient (k) of the films have been calculated by using relation

$$k = \alpha\lambda/4\pi \qquad (4)$$

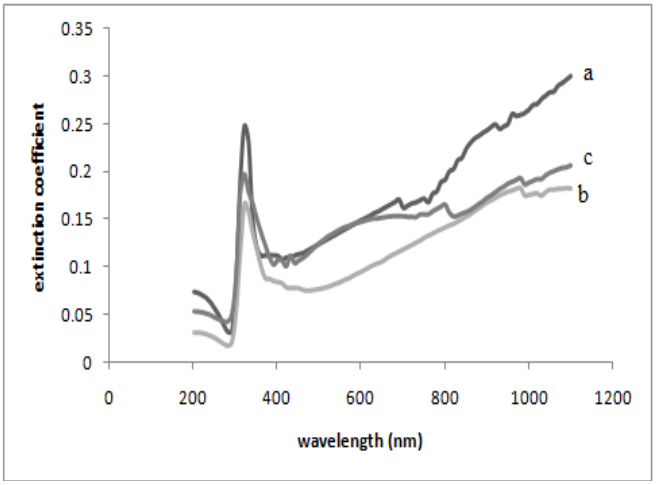

Fig 5. Wavelength dependence of extinction coefficient (k) of TiO_2 films of thickness (a) 100nm (b) 200nm (c) 300nm deposited onto a glass substrate.

Fig 5 shows variation of extinction coefficient with wavelength (λ) for the TiO_2 films with different thickness deposited onto a glass substrate and found to be lie in the range 0.021 – 0.29.

5. Conclusions

The present study comprises of structural and optical properties of TiO_2 films prepared by sol gel spin coating technique onto glass substrate with different thickness. The XRD pattern obtained for spin coated TiO_2 films deposited onto a glass substrate kept at different thickness show the presence of sharp and well resolved peak along the (121) plane, which confirms the formation of brookite phase of TiO_2. It is observed that intensity of the peak increases with increase in thickness of the films, hence FWHM decreases, which reveals the increase in crystallinity and better crystal perfection of thick films. SEM studies indicate uniformly distributed grains in TiO_2 films. It is observed that the dimensions of the crystallites increase with increase in the thickness of the film. The absorption spectra of the films recorded at room temperature show an absorption hump at wavelength 320nm. Observation reveals that absorbance increases with increase in thickness of the films. The optical band gap of the films deposited onto glass substrate of different thickness is found to lie in the range 3.35-3.55 eV. The extinction coefficient of the films lies in the range 0.021-0.29. These observations confirm that spin coating technique can be scaled up to industrial level for preparing TiO_2 films, which has potential for its application as window material for solar cell devices.

References

[1] D.S. Ginley, C. Bright, MRS Bulletin, **25**, 15 (2000).

[2] E. Fortunato , D. Ginley, H. Hosono, D.C., Paine, MRS Bulletin, **32**, 242 (2007).
[3] S. Lany, A. Zunger, Physical Review Letters, **98**, 045501 (2007).
[4] John D. Perkins & David S. Ginley, Photovoltaics International journal.**3**, 94 www.pv-tech.org (2009)
[5] D. Lucaa, L. S. Hsu, J. Optoelectron. Adv. Mater. **5**, 835 (2003).
[6] Diana Mardare and G. I. Rusu**,** Materials Science and Engineering B**, 75**, 68 (2000).
[7] Claudian Georgescu , SPIE, Proceedings, **2461**, 594 (1995).
[8] Juho-Pertti Jalava, Lauri Heikkila, Oskari Hovi, Reino Laiho, Erkki Hiltunen, Arvi Hakanen, Harri Harma, Ind. Eng. Chem. Res., **37**, 1317 (1998).
[9] Flores Mendoza, M.A. Castanedo, R. Perez., Delgado Torres, J. Marquez Marin, O. Zelaya Angel, Thin Solid Films,**51**, 3890 (2008).
[10] Jiaguo Yu, Xiujian Zhao, Qingnan Zhao, Journal Of Materials Science Letters, **19**, 1015 (2000).
[11] I.N. Kuznetsova, V. Blaskov, I. Stambolova, L. Znaidi, A. Kanaev Materials Letters, **59,** 3820 (2005).
[12] J. Bardeen, F. J. Blatt, L.H. Hall, Photoconductivity Conf., Ed. R. Breckenridge, B. Russel and T. Hahn, John-Wiley, New York (1956).
[13] Chen Yang, Huiqing Fan, Xi. Yingxue, Jin Chen, Li.Zhuo Applied Surface Science, **254**, 2685 (2008).

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