

Preparation and characterization of porous TiO₂ thin films by sol-gel method for Extremely Thin Absorber-ETA solar cell applications

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(Received:24.05.2013; Accepted:10.06.2013)

Abstract

Nanoporous TiO₂ thin films have been widely used as window and n-type material for the Extremely Thin Absorber-ETA solar cells. Nano scale titanium dioxide (TiO₂) films were deposited on the surfaces of bare glass and Indium Tin Oxide (ITO) coated glass substrates using spin coating method. The effect of different spinning rates on the surface structures and properties of the films was investigated. The surface morphology of nanostructure TiO₂-coated films were characterized by Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and BET studies. UV-Vis spectroscopy and dark I-V measurement were also performed to get the information about the optical and electrical properties. The test results proved that; by changing the spinning rates homogeneous anatase films of TiO₂ with different thicknesses can be produced. The investigation show that TiO₂ porous films obtained by spin coating method with 8000 rpm-spinning rate have the appropriate properties for ETA solar cell study.

Keywords: Thin film, TiO₂, Spin coating , XRD, Band gap, Transmittance

Çok ince Soğurucu – ETA güneş gözelerine uygulamaları için gözenekli TiO₂ ince filmlerin sol-jel metodu ile üretilmesi ve karakterizasyonu

Özet

Nano-gözenekli TiO₂ ince filmleri, Çok İnce Soğurucu - ETA güneş gözeleri için pencere katmanı ve n-tipi malzeme olarak yaygın bir şekilde kullanılmaktadır. Nano boyutlu titanyum dioksit (TiO₂) filmleri işlenmemiş cam ve indiyum kalay oksit (ITO) kaplı cam alttaş yüzeylerine döndürerek kaplama (spin coating) yöntemi kullanılarak büyütülmüştür. Farklı döndürme hızlarının yüzey yapıları ve ince filmlerin özellikleri üzerine etkileri incelenmiştir. Nano-yapıda TiO₂ kaplı filmlerin yüzey morfolojisi Atomik Kuvvet Mikroskobu (AFM), Taramalı Elektron Mikroskobu (SEM), X-Işını Kırınımı (XRD) ve BET çalışmaları ile karakterize edilmiştir. Ayrıca, UV-Vis spektroskopisi ve karanlık I-V ölçümleri optik ve elektriksel özellikler hakkında bilgi edinmek için gerçekleştirilmiştir. Deneme sonuçları, döndürme hızlarını değiştirerek farklı kalınlıklarda homojen anataz TiO₂ ince filmlerinin üretilbildiğini göstermektedir. Araştırmalar 8000 rpm döndürme hızı ile döndürerek kaplama metodu ile elde edilen gözenekli TiO₂ filmlerin ETA güneş gözeleri çalışması için uygun özellikler taşıdığını göstermektedir.

Anahtar Kelimeler: İnce Film, TiO₂, Döndürerek Kaplama, XRD, Bant aralığı, Geçirgenlik

1. Introduction

One of the most effectual ways to harvest energy from the sun, which is the primary and renewable source of energy, is the use of photovoltaic effect in solar cells [1]. Over the last few years new designs have been proposed for photovoltaic devices, which would allow higher conversion efficiencies and also the use of less expensive materials or processes [2–5]. Recently a new type of cell with extremely thin absorber, the Extremely Thin Absorber layer – ETA solar cell is explored [5, 6].

ETA solar cells consist of an extremely thin absorber, which is sandwiched between interpenetrating transparent nano-structured n-type semiconductor and a transparent void filling p-type semiconductor with a metallic back contact [7, 8]. The concept of ETA solar cell is similar to those cells, which use a dye for light absorption and are embedded between semiconductors [9, 10].

In ETA cells [11], since using an absorber layer with a thickness of several nanometers the probability of electron recombination is reduced. Highly structured p–n heterojunctions are needed to provide sufficient absorption of the light [12], so the scattering at the internal interfaces of the structure will increase and consequently optical absorbance is enhanced.

For ETA solar cells, the most frequently used materials as n-type, have been porous TiO_2 [13,14] and ZnO nano-wire films [15,16]; while as p-type material, CuSCN [14,17] and ZnTe [18] have been used. As the thin inorganic absorber layer, the semiconductor materials such as CdTe [7,15], a-Si:H [16] and CuInS_2 [17] have been used.

The unique transport properties and observed low charge recombination rates of TiO_2 , as the n-type semi-conducting electron transport layer, lead to widespread use in ETA solar cells; photo-catalysis and dye sensitized solar cells, giving highest efficiencies among

most semiconductors such as ZnO , SnO_2 , etc. Most of dye sensitized solar cell applications require thick films of TiO_2 mesoporous networks. However in ETA solar cells, due to smaller diffusion lengths and employment of high extinction coefficient absorber layers, thin films of porous structures seem to be advantageous. Various deposition techniques can be employed for thin films production like e-beam PVD [19], spray pyrolysis [20], electrophoretic deposition [21] or Successive Ionic Layer Absorption and Reaction (SILAR) [22]. However, most TiO_2 layers are produced by soft chemical route or sol-gel techniques like spin coating [23,24] and dip coating [25,26] including in situ deposition of TiO_2 layers with nano-crystalline structure by means of hydrolysis and condensation reactions of a precursor solution of metal salts or alkoxides on substrates followed by thermal annealing. In sol-gel, such coatings yield thin films of dense nanocrystalline structures or macropores [27] with limited porosity for solar cell applications. Addition of block copolymers into the coating precursor solution is an alternative strategy to improve mesoporosity giving ordered mesopores in the film for enhanced surface area [28, 29]. Although the most common technique to deposit TiO_2 layers is screen printing [30] or doctor blade [31] of viscous pastes containing the pre-synthesized TiO_2 particles and binders, only thick films can be formed using these methods.

In this work, very thin layers of highly porous TiO_2 nanoparticle films were deposited on glass and ITO coated glass substrates for ETA solar cell applications with a modified, easy to prepare low viscosity paste using spin coating for different spinning rates. Thickness measurements, optical, electrical and morphological characterizations were conducted by SEM, AFM, UV-Vis spectrometer, BET, XRD and dark I-V techniques.

2. Experimental

TiO₂ thin films were deposited using a low viscous paste containing terpineol, ethyl cellulose and a commercial TiO₂ dispersion, Degussa VP Disp LE 2730X containing 30% wt. TiO₂ nanoparticles in isopropanol. Ethyl cellulose was first dissolved in isopropanol and mixed with the TiO₂ dispersion. This mixture was homogenized by a magnetic stirrer and subsequent ultrasonic treatment using an ultrasonic horn for 15 minutes. After addition of terpineol and repeating homogenization, isopropanol was evaporated by a rotary evaporator at 40 °C. Ratios of the ingredients are fixed for every deposition which is 2:1:28 for TiO₂, ethyl cellulose and terpineol, respectively. This formulation is a modified screen printing paste used for mostly dye sensitized solar cells [32]. Resulting is a low viscous paste, which was no more homogenized and used for spin coating. Bare glass and ITO coated glass substrates were firstly cleaned by deionized water and isopropanol in an ultrasonic bath and coated by spin coating at 2000, 5000 and 8000 rpm for 1 min and only for 1 run, in a clean room environment. After drying the substrates at 120 °C for 5 minutes, these films were annealed for 30 min in nitrogen flow at 450 °C.

The thicknesses of the samples were measured by using a FEI Quanta 400 FEG model Scanning Electron Microscope (SEM) following the depositions and found to be in different thicknesses for different spinning rate values. X-ray diffraction measurements were performed by using a Rigaku Miniflex X-ray Diffraction (XRD) system equipped with CuK α radiation of average wavelength 1.54 Å. Optical characterizations of the samples were carried out by taking transmittance measurements using LAMBDA 950 UV/Vis/NIR Spectrophotometer over the wavelength range of 200-2000 nm. For the electrical measurements, ohmic contacts were produced by the evaporation of high-purity

aluminum through a dot contact mask in a metallic evaporation system. Also the ohmic nature of contacts was confirmed by measuring I-V characteristic with the reversal of the applied current. The resistance values of the deposited films were obtained using the I-V variations.

In order to analyze the specific surface areas on the samples, Quantachrome Corporation, Autosorb-6 (BET) system was used. The AFM imaging for the topography of TiO₂ surfaces was realized by using a Vecoo MultiMode V AFM system.

3. Results and Discussion

3.1. Structural Properties

In order to determine the diffraction patterns; also the phases and orientations of the deposited TiO₂ thin films on the glass and ITO coated glass substrates, XRD measurements were used. Besides, these analyses helped to observe the possible changes in the film structures, which depend on the substrate material differences and speed of the spin coating process. The XRD analysis of the powder is given in Fig.1; and analyses of the thin films are given in Fig.2 and 3, for the glass and ITO coated glass substrates, respectively.

According to Fig.1, the powder showed corresponding crystalline phases and had nanoparticle structure. The XRD pattern of powder showed anatase phase (JCPDS 21-1272 Anatase) with preferred orientation along (1 0 1) plane with diffraction angle 2 θ of about 25° [33]. Although the anatase is the desirable form of TiO₂ for solar cell applications, very small amount of rutile (JCPDS 73-1765 Rutile) is presented in the structure, however it is negligible.

XRD patterns of TiO₂ films coated on glass substrates by spin coating deposition technique are presented in Fig.2, for three different spinning rates which are 2000, 5000 and 8000 rpm. The deposited films prepared on bare glass

substrates were found to be amorphous for all different spinning rates.

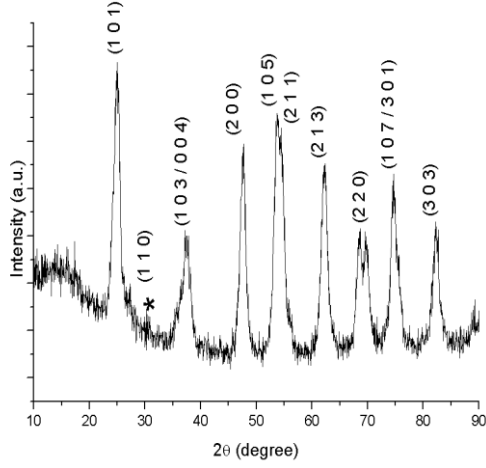


Figure 1. XRD patterns of the TiO_2 powder, peak indicated by ★ is due to rutile phase

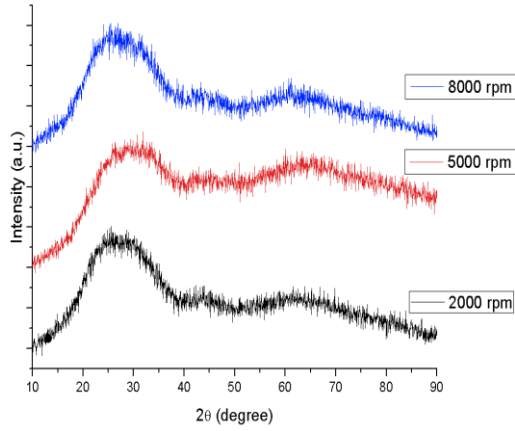


Figure 2. XRD patterns of the TiO_2 films deposited on the glass substrates

The XRD patterns of the TiO_2 films grown on ITO coated glass substrates together with that of ITO coated glass illustrated in Fig.3, show the peaks belonging to the anatase phase. Moreover, with the increase in the coating speed of the ITO coated on glass films, the diffraction peaks become sharper.

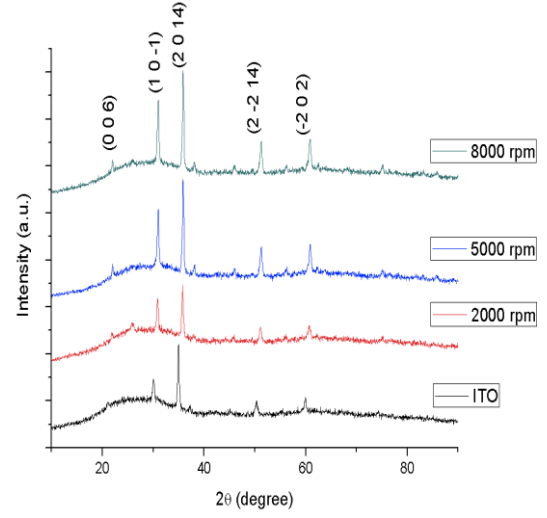


Figure 3. XRD patterns of the TiO_2 films deposited on the ITO coated glass substrates

In fact, it is observed that there was strong effect on XRD patterns of these spin-coated TiO_2 films by the crystalline characteristics of substrate material. Therefore, the difference in crystalline nature of these films is attributed to the difference in the nature of the substrates.

The average microcrystalline grain size d was estimated from the XRD pattern of powders using Scherrer's formula [34] expressed as;

$$D = \frac{K}{b \cos \theta} \quad (1)$$

where K is the shape factor equal to 0.94 [35], λ is the wavelength of X-rays, β is defined as the diffraction peak width at half height (FWHM), and θ is the diffraction angle (Fig.1). Therefore, the crystallite size of powders calculated from the XRD pattern using the Eq.1 was about 24 nm.

Specific surface area of the powders used in this work is $108 \text{ m}^2/\text{g}$ calculated from the BET gas adsorption measurements with an average pore size of 17 nm. This degree of specific surface area is suitable for nano-crystalline and

solar cell applications. Assuming spherical particles, the average particle size [36] is calculated from the expression;

$$D = \frac{6000}{S_{sp} \cdot r_a} \quad (2)$$

In Eq.2, D is the particle size in nm, S_{sp} is the specific surface area of the powders in m²/g and r_a is the density of TiO₂ (4.23 g/cm³). The calculated value of 48 nm of BET measurement is twice the crystallite size obtained from XRD measurements; this difference is attributed to the slightly agglomerated nature of the powder in BET measurement.

3.2. Morphological Properties

High-resolution SEM images of spin-coated thin films are given in (Fig.4 and 5). Films are in the form of a network of high porosity inter-connected nano particles, which approximately have a pore size ranging between 50-100 nm, and the particle size around 20 nm. These results are consistent with X-ray measurements confirming that the films have high porosity and high surface area which is a critical factor for most nano-crystalline solar cell structures demanding binding sites for absorber layers and open pores provide enough space for p type penetration.

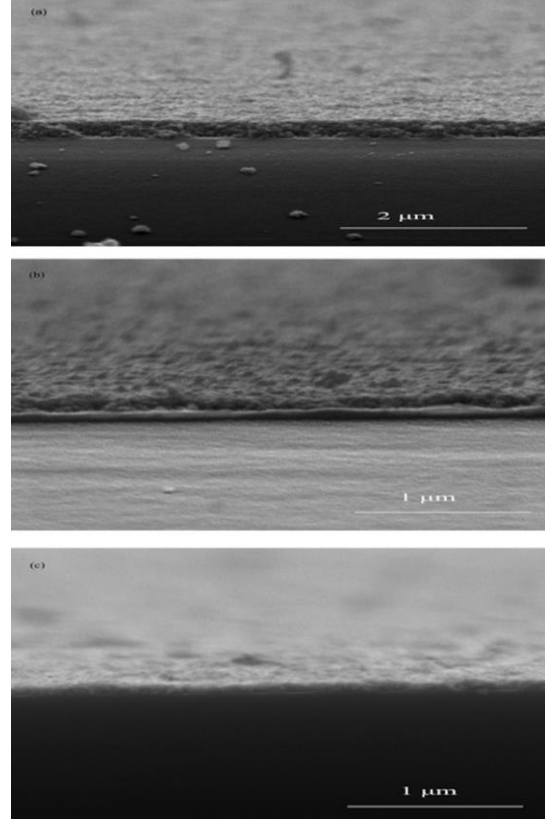


Figure 4. SEM micrographs of TiO₂ films coated on the glass substrates using coating speeds of (a) 2000, (b) 5000 and (c) 8000 rpm

Cross-sectional images reveal that by changing the spin rate simply, it is possible to obtain thin films with different thicknesses down to 80 nm. Films are homogeneous and crack free on the entire surface. Also there are no visible agglomerates on the surface, which shows a proper homogenization of the paste used in this study.

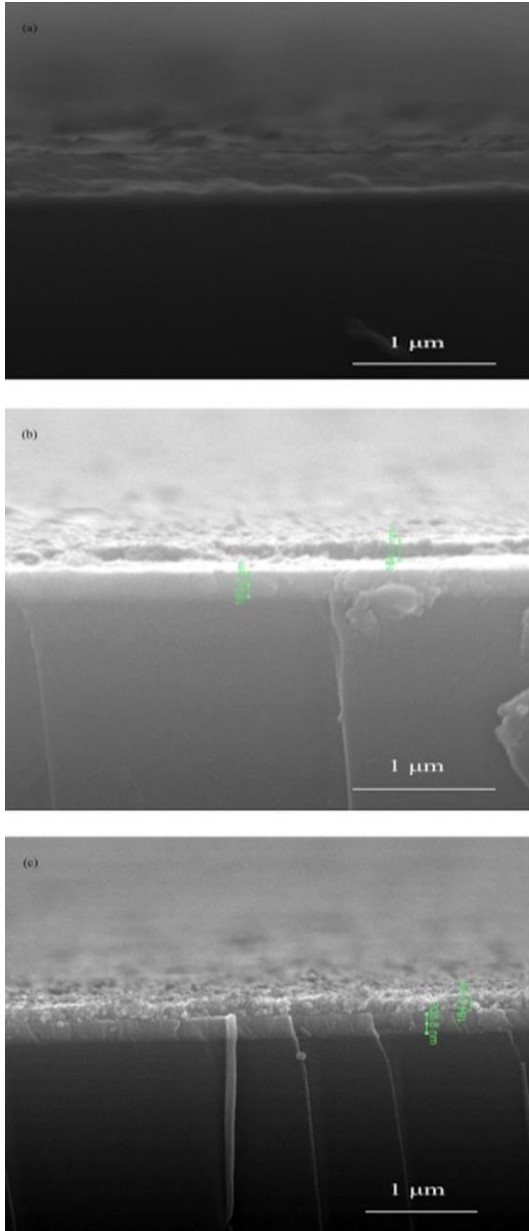


Figure 5. SEM micrographs of TiO₂ films coated on the ITO substrates using coating speeds of (a) 2000, (b) 5000 and (c) 8000 rpm

Although no significant difference was noticed regarding the morphology of the films on both glass and ITO coated glass substrates at different spinning rates; a better Crystallinity and a slight increase in the grain size was observed using XRD and SEM results for the TiO₂ films obtained using 8000 rpm spinning rate. The results of AFM measurements are shown in the

Fig.6 and 7 and Table 1 summarizes the roughness values of the films.

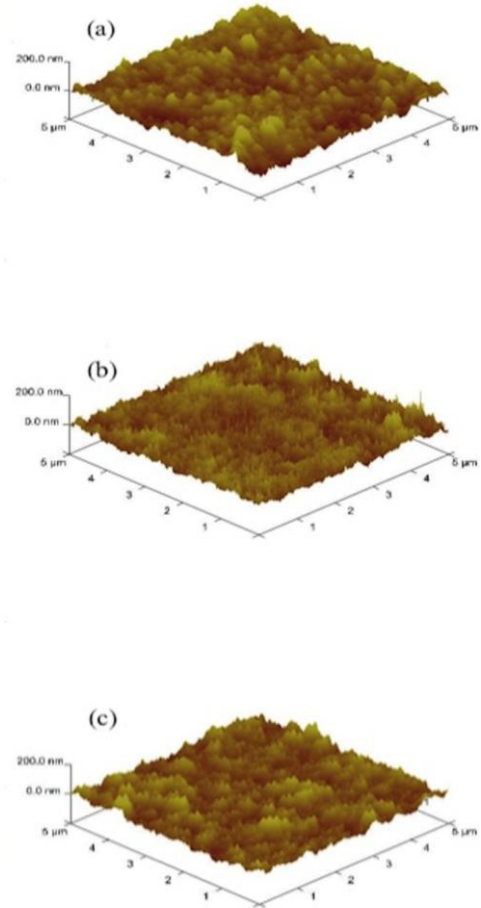
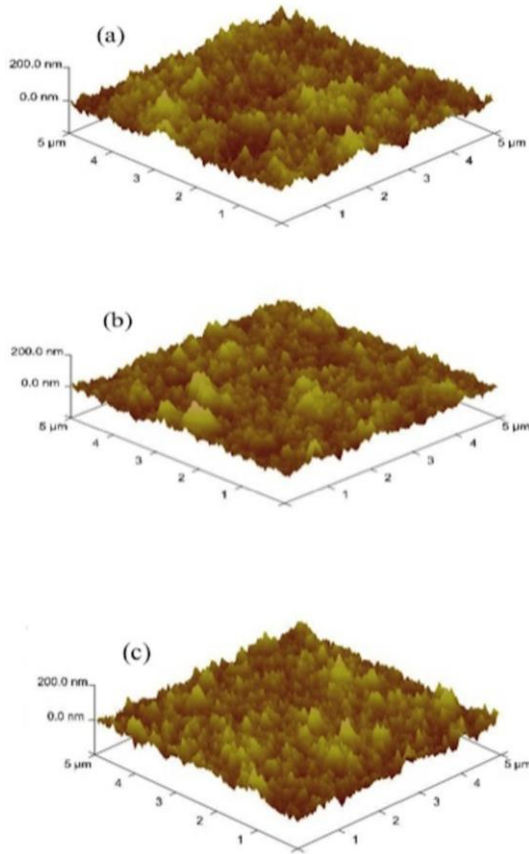


Figure 6. AFM images for films deposited on the glass substrate using coating speeds of (a) 2000, (b) 5000 and (c) 8000 rpm

A high-resolution AFM image reveals that, in consistent with SEM results, films are porous and have a nano-particulate structure. Particle sizes are around 25-30 nm and pore sizes are around 50-100 nm. There are no large voids or deviations in the homogeneity of the films as indicated by the roughness values, which are around 20 nm for all samples indicating that the morphology of the films are independent of the spinning rates and reproducible results can be obtained for different thickness values.

Table 1. The roughness values of the coated films and substrates

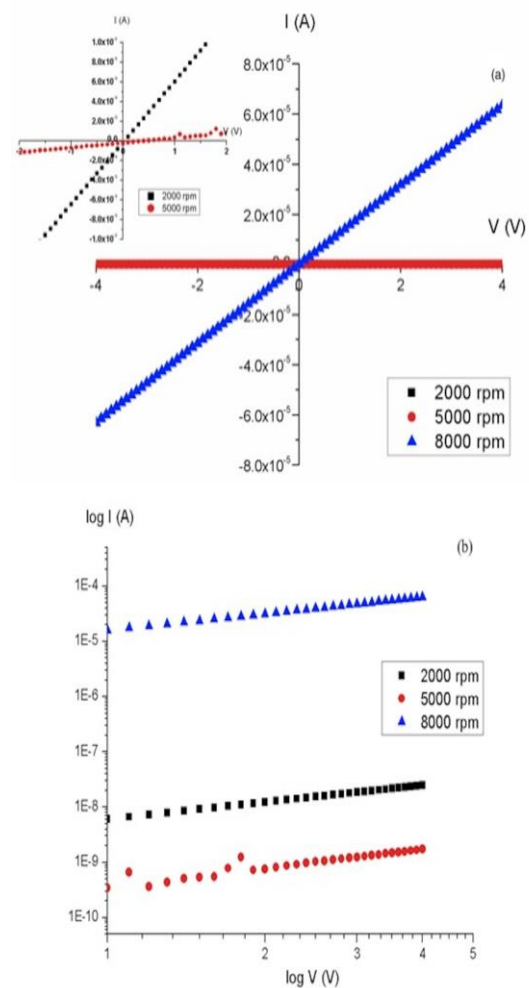
Sample	Glass substrate	ITO coated glass substrate	TiO ₂ coated on glass 2000rpm	TiO ₂ coated on glass 5000rpm	TiO ₂ coated on glass 8000rpm	TiO ₂ coated on ITO 2000rpm	TiO ₂ coated on ITO 5000rpm	TiO ₂ coated on ITO 8000rpm
Roughness value	1.61 nm	2.86 nm	18.9 nm	17.1 nm	18 nm	20.8 nm	18.9 nm	20.3 nm

**Figure 7.** AFM images for films deposited on the ITO coated glass substrate using coating speeds of (a) 2000, (b) 5000 and (c) 8000 rpm

3.3. Electrical Properties

In order to have information about the electrical conductivity of the produced TiO₂ films, the current-voltage measurements were performed between the two metallic contacts applied to the surface of the films coated on glass substrates.

The I-V variations of the films for different spin rates are illustrated in Fig.8 a and b, in linear and Log-Log scale respectively.

**Figure 8.** Room temperature dark I-V measurements for the TiO₂ films coated on the glass substrate in terms of coating speed: (a) linear and (b) logarithmic plot

As observed from the figure, the lowest resistance value was obtained for the film coated

at a spin rate of 8000 rpm with a calculated resistivity value which is almost 10^4 times lower than those obtained for the films coated at a spin rate of 2000 and 5000 rpm (Table 2).

Table 2. The resistivity values of the TiO₂ films

Sample Substrate	Glass		
Coating speed (rpm)	2000	5000	8000
Resistance (Ω)	16×10^7	2×10^9	5×10^4
Resistivity ($\Omega \cdot \text{cm}$)	2.6×10^3	4.8×10^3	0.21

3.4. Optical Properties

The room temperature transmission measurements were performed for the optical characterization of the films deposited on glass and ITO coated glass substrates at different spin rates. In the wavelength region of 200-2000 nm, T % (transmission) versus λ (wavelength) variations of all the samples is shown in Fig.9 and 10.

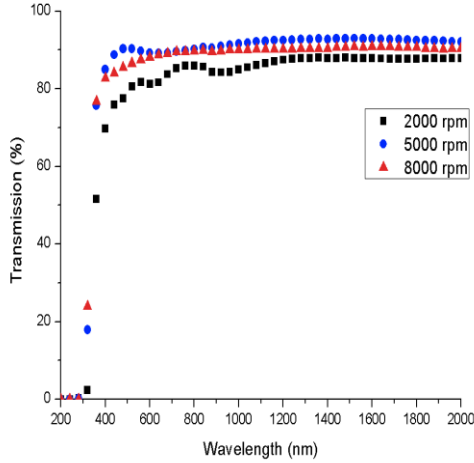


Figure 9. Transmission spectra of the TiO₂ samples on glass substrate

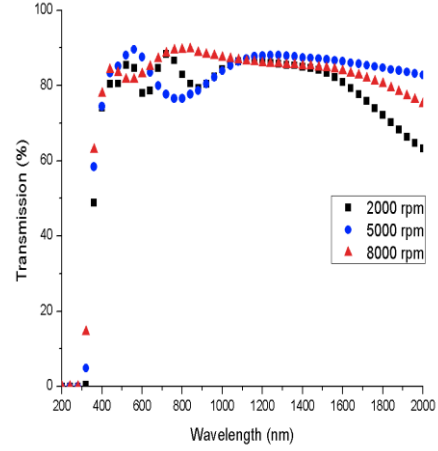


Figure 10. Transmission spectra of the TiO₂ samples on ITO coated glass substrate

According to Fig. 9 and 10, the films maximum transmittance of about 90% at the wavelength interval of around 375-600 nm. A shift was observed in this wavelength region to 425-850 nm for the samples deposited on ITO coated glass substrate, which indicates a good transmittance of visible light. The transmittance of UV and visible region in the range of 300–850 nm is considerably reduced to a level below 5%, revealing the light-shielding effect of the Ti coating [37]. Moreover, the relatively high transmittance of the film indicates low surface roughness and good homogeneity.

Absorption coefficient is calculated by using the relation;

$$a = -\left(\frac{1}{d}\right) \ln\left(\frac{I}{I_0}\right) \quad (3)$$

Where d is the thickness, I is the intensity of transmitted light, and I_0 is the incident light perpendicular to the surface of the sample [38].

For a direct band gap, the absorption coefficient α is related to light frequency according to the following formula;

$$(\alpha h\nu) = A(h\nu - E_g)^{\frac{1}{2}} \quad (4)$$

where A is an energy-independent constant and E_g is the forbidden band gap energy [39,40]. Therefore, from the plot of $(\alpha h\nu)^2$ versus $h\nu$ (Tauc plot) (Fig.11 and 12), the band gap values can be defined by extrapolation of the straight line on the energy axis.

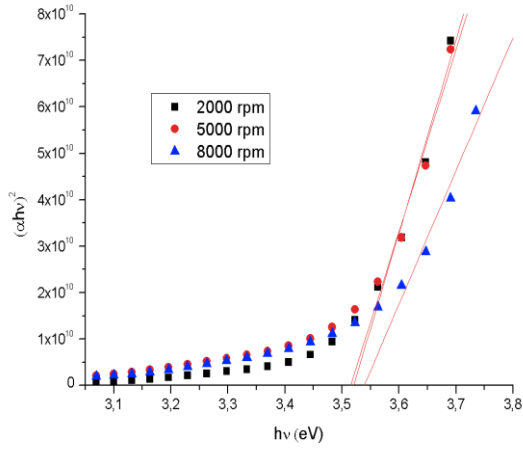


Figure 11. Tauc plot of the TiO₂ samples on glass substrate

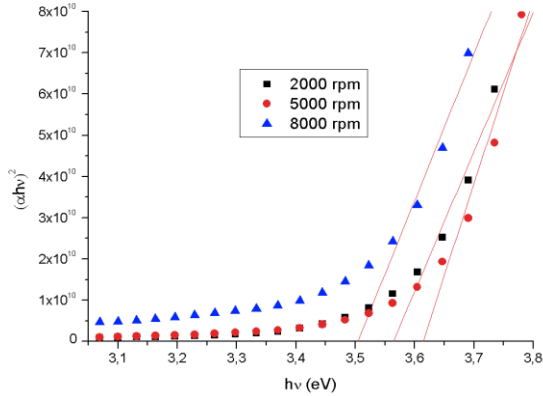


Figure 12.TIF: Tauc plot of the TiO₂ samples on ITO coated glass substrate

The films deposited on glass and ITO substrates, exhibited direct band-gap energy of around $E_g = 3.50 - 3.60$ eV. These values are in consistent with those reported elsewhere. [41, 42]

4. Conclusion

In this work, a modified TiO₂ paste was prepared for deposition of very thin layers with high porosity and nanoparticulate nature for extremely thin absorber solar cell applications. By using a commercially available TiO₂ source and simple spin coating technique, layers of nanoporous TiO₂ matrix could be easily deposited. As a result of XRD analyses, increasing the speed of coating made a gradual crystallization of the material to the anatase component in the films deposited on the ITO coated glass substrates. The morphological and structural characterizations indicated the homogeneous and crack free anatase thin films with different thicknesses down to 80 nm can be easily prepared by simply changing the spin coating rate which is not possible with widely used screen printing or doctor-blade techniques. Electrical characterization showed that the electrical resistivity of the films decreases by a factor of 10^4 , when the spin rate increase to 8000 rpm resulting the resistivity value of with a value of $2.1 \times 10^{-1} \Omega \cdot \text{cm}$. The optical characterization through the transmission studies indicated direct band-gap of the TiO₂ films with the average value of $E_g = 3.5 - 3.6$ eV. The structural, optical and electrical characterization results in this study, give the indication of appropriate use of TiO₂ nanoporous thin films coated by the sol-gel method at the spin rate of 8000 rpm, for ETA solar cell applications.

Acknowledgement

This work has been supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under Graduate Scholarship Programme for International Students. The authors would like to express their sincere thanks to Prof. Dr. C. Ercelebi and Prof. Dr. M. Ozenbas for their assistance.

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