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Study of spray deposited titanium dioxide films

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ABSTRACT

The titanium dioxide films have been obtained by spray pyrolysis technique on to the glass substrates kept at different temperature (300- 400^{0C}) .The conditions have been optimized to obtain quality films. Films so obtained have been characterized for their structure through x-ray diffractograms. Optical absorption studies of the films have been made through UV-Visible spectroscopy in the spectral range 300 -1100 nm. Effect of substrate temperature on the structure and optical properties of these films has been studied. Results indicate that the films so obtained are promising candidates for solar cells.

Key words: Spray pyrolysis, TiO_2, optical properties.

INTRODUCTION

Over the last few decades, titanium dioxide (TiO_2) has been widely investigated recently for its interesting optical properties, electronic properties and good stability in the adverse environment. For its high refractive index, wide band gap and chemical stability, titanium dioxide has attracted considerable attention for its potential applications in optical components including solar cells [1], electro-chromic displays [2] and optical filters [3]. Polycrystalline TiO2 films are used for a variety of applications such as optics industry [4], dye sensitized solar cells [5], dielectric applications [6], self cleaning purposes [7] and photo-catalytic layers [8]. The highly transparent TiO2 films have been widely used as antireflection coatings for increasing the visible transmittance in heat mirrors [9]. As a dielectric material, TiO2 is one of the mostly used materials for the purpose of antireflection coatings [10-13]. TiO2 can exist as an amorphous layer and also in three crystalline phases: anatase (tetragonal), rutile (tetragonal) and brookite (orthorombic) but its orientations in thin-film form depend upon the conditions and parameters of the fabrication method [14].Only rutile phase is thermodynamically stable at high temperature. The refractive index at 500 nm for anatase and rutile bulk titania is about 2.5 and 2.7 respectively [15]. There are many deposition methods used to prepare TiO2 thin films, such as electron-beam evaporation [16], ion-beam assisted deposition [17], DC reactive magnetron sputtering [8], RF reactive magnetron sputtering [5, 18], Sol-gel methods [19, 20], chemical vapor deposition [21] and plasma enhanced chemical vapor deposition [6]. The properties of the titanium dioxide films depend not only on the preparation techniques but also on the deposition conditions. Heat-treatment is one of the utilized ways to obtain better optical properties of TiO_2 films [14, 22].

Sol–gel techniques have been extensively used by dipping substrates in precursor solutions of titanium isopropoxide ($C_{12}H_{28}O_4Ti$) with a suitable molar ratio of different components of solution. However, it has recently been demonstrated that spin-coating can be adapted as an alternative to dip-coating for deposition of thin TiO2 films from a similar sol precursor on to glass substrates [23]. The sol-gel technique (spin coating, dip coating) has distinct advantages over the other methods as the structural properties of the films can be carefully controlled due to the

usage of the liquid precursors and offers the possibility of relatively low cost, large-scale production of thin films. Recent work has identified significant interactions between process parameters such as withdrawal rate, sol concentration and the number of coating layers and their effects on structural, optical and electrical properties of sol-gel derived TiO, films [24].

In this paper, we present a study of the optical properties of titanium dioxide films obtained on glass substrates using a low cost spray pyrolysis technique taking titanium isopropoxide based precursor solution. The effects of substrate temperature on structure and optical properties have been investigated.

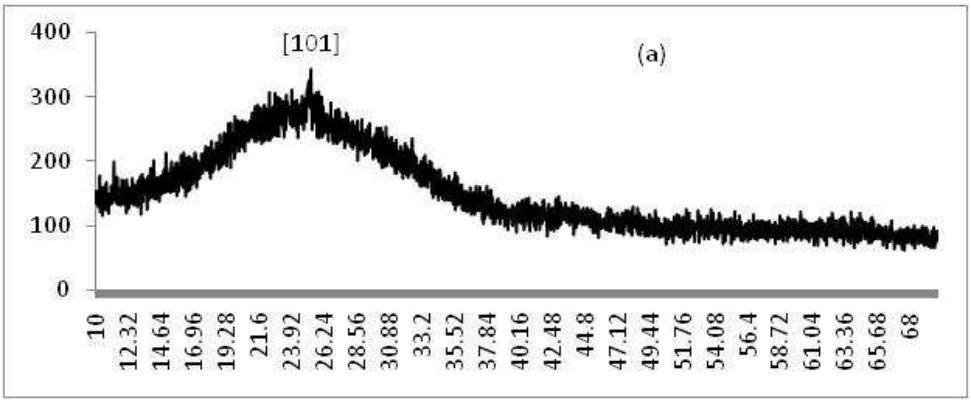
MATERIALS AND METHODS

Chemically and thermally stable films of titanium dioxide were prepared using the spray pyrolysis technique. Microscope glass slides were used as the substrates for thin films. Prior to deposition, the glass slides were sequentially cleaned in an ultrasonic bath with acetone and ethanol. Finally they were rinsed with distilled water and dried. The precursor solution was prepared by mixing 2.5 ml. Titanium (IV) isopropoxide, 80 ml. of water, 20 ml. of acetic acid 20 ml. of ethanol and 1 ml. of nitric acid . The solution so obtained was stirring at 50 ^{0}C temperature for three hours in an air tight container. Fixed ratio of the precursor solution and air was made to spray in form of mist from ultrasonic nebulizer on to the open air heated substrates. The substrate temperature was varied between 300 to 400^{0}C and substrate height was kept 3.7 cm for each deposition. The deposition time was fixed two minutes for each deposition. The films were then cooled down to room temperature in open air. The crystalline properties of the titanium dioxide films were analyzed by an X-ray diffractometer (Model-D5000, Siemens) using CuK_α radiations (λ=0.15405 nm) and operating at an accelerating voltage of 40 kV and an emission current of 30 mA. Data were acquired over the range of 2θ from 15 to 70^o at scanning speed of 5^o min^{-1}. The XRD method was used to study the change of crystalline structure. The UV-visible-IR optical transmission spectra of titanium dioxide thin films were recorded by a double-beam spectrophotometer in the range of 300-1100 nm. The measurements were taken at a normal incidence using a reference blank substrate. From the transmittance and absorbance spectra, Swanepoel [25] methods were used to calculate the optical constants, absorption coefficient and optical band gap of the films. The thickness of the thin films were estimated to be 87 nm by max-min method, using the formula:

$t = \lambda_1 \lambda_2 / 4n (\lambda_2 - \lambda_1)$,
Where
't' is the thickness of the film, λ_1 and λ_2 are the wavelengths which corresponds to the maxima and minima of the transmittance spectra and 'n' is the refractive index to titanium dioxide.

RESULTS AND DISCUSSION

Structure:
The X-ray diffractogram of titanium dioxide films grown at different substrate temperatures (300 to 400 ^{0}C) has been shown in figure 1 (a-c). The d values of the films are compared with the literature data to confirm the structure of titanium dioxide and found to be in good agreement thus confirming the formation of titanium dioxide film on the substrate.



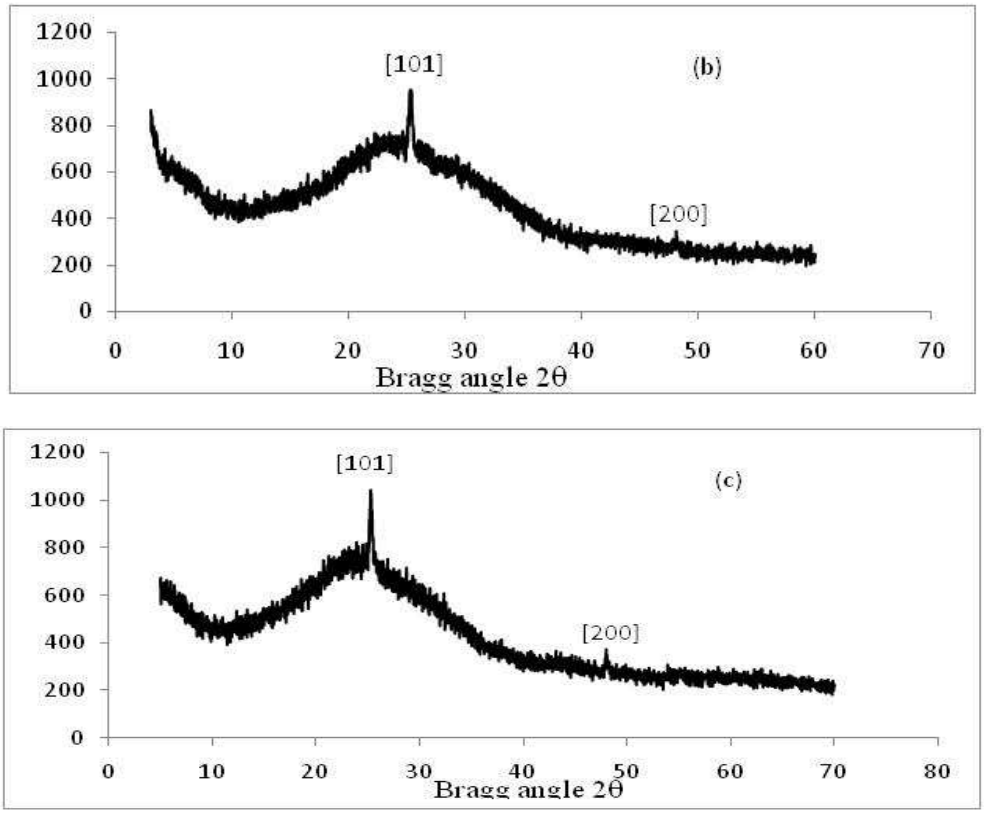
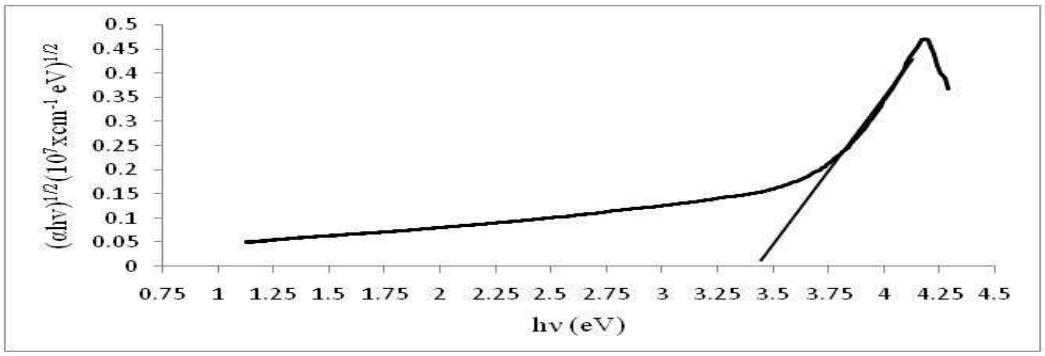
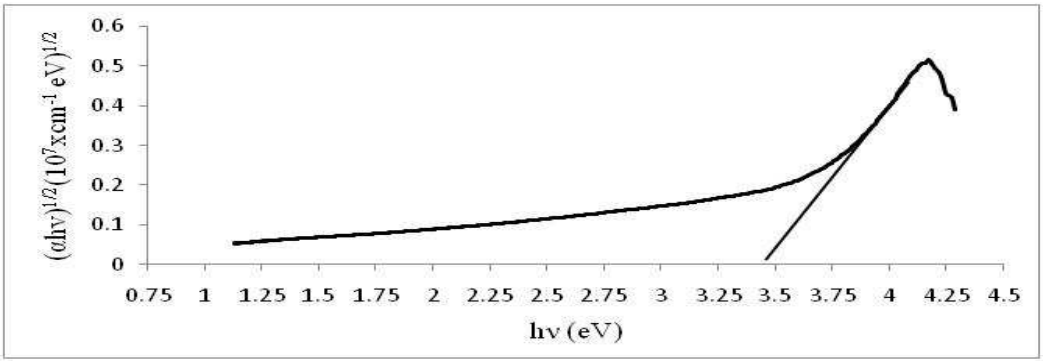


Fig. 1 (a,b,c) : XRD pattern for titanium dioxide films grown at (a) 300 ^{0}C (b) 350 ^{0}C and (c) 400 ^{0}C

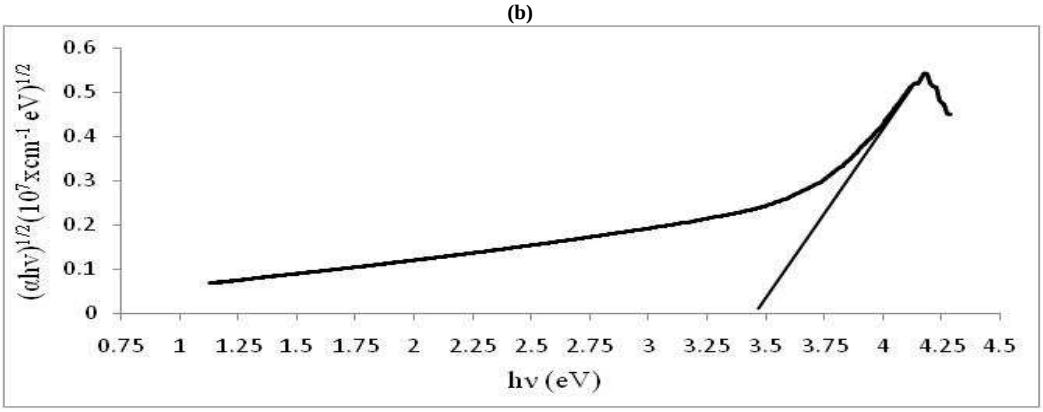
The films are observed to have a preferential crystallographic texture in the [101] direction corresponding to the Bragg angle $2\theta = 25.3^0$. However, X-ray diffractogram shows the presence of weak intensity peaks with orientation [200] with $2\theta = 48.1^0$ that is also in agreement with the previously reported values**.** The films deposited at higher temperatures show comparatively intense peaks. Also decrease in full width measured at half maxima (FWHM) of diffraction peaks has been noticed, thus suggesting a high degree of crystallinity with increase in substrate temperature.



(a)



(b)

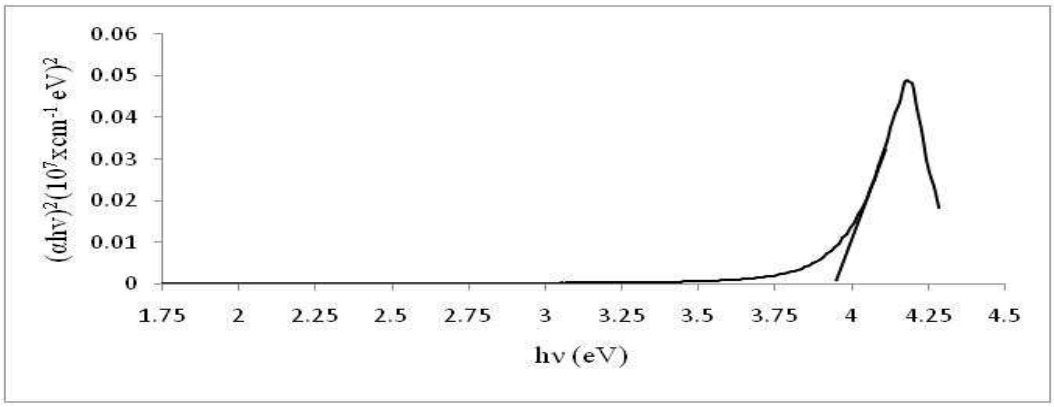


(c)

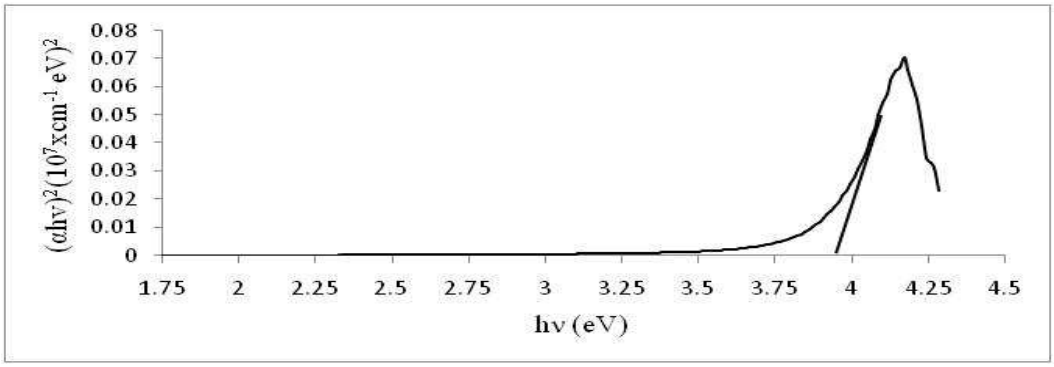
Fig. 2 (a,b,c): $(\alpha h\nu)^{1/2}$ Vs hν for the titanium dioxide films grown at (a) 300 ^{0}C (b) 350 ^{0}C and (c) 400 ^{0}C

Optical Properties:

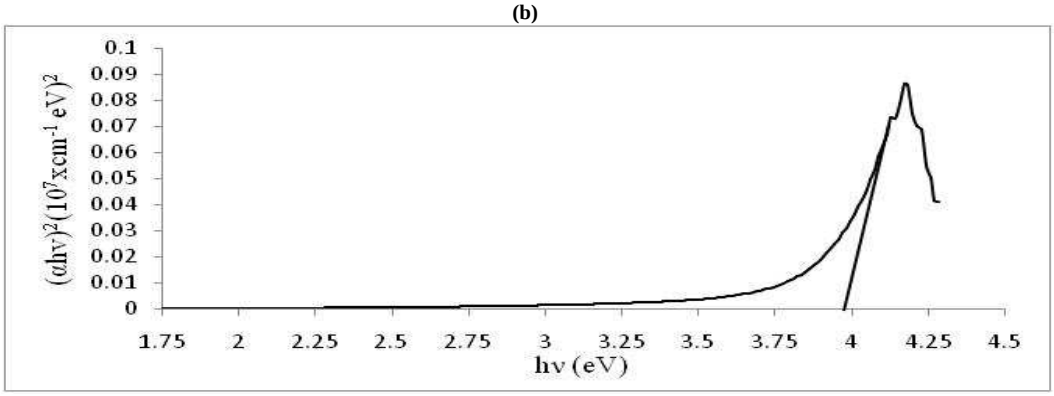
The absorption coefficient of titanium dioxide films deposited on glass has been determined over the energy range 1.1-2.4 eV, which correspond to an absorption edge in the lower energy region of the transmittance spectra of the films taken over 300-1100 nm range. This absorption edge of the titanium dioxide has been examined in terms of a direct transition using the equation of Bardeen et al [27], stating that: $\alpha h\nu = B(h\nu - E_g)^n$ where α is the absorption coefficient, hν is the photon energy, E_g is the optical band gap, B is a constant which does not depend on photon energy and n has four numeric values (1/2 for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions).



(a)



(b)



(c)

Fig. 3 (a,b,c) : $(\alpha h\nu)^2$ Vs hν for the titanium dioxide films grown at (a) 300 ^{0}C (b) 350 ^{0}C and (c) 400 ^{0}C

In this work, direct and indirect band gap was determined by plotting $(\alpha h\nu)^2$ vs. hν and $(\alpha h\nu)^{1/2}$ vs. hν curves respectively, with the extrapolation of the linear region to low energies. From Figs. 2 and 3**,** it has been observed that both indirect and direct optical band gap increases from 3.40 eV to 3.47 eV and from 3.90 eV to 3.97 eV respectively with the increase in substrate temperature. This increase in band gap energy may be attributed to the improvement of crystallinity of anatase phase with the increase in substrate temperature and due to the fact that high substrate temperature favors the growth of larger crystallite size and exhibit more ordered structure, which gives comparatively less contribution to the absorption [28] . Results are in good agreement with the findings of Amor et al. [16,17,18]. The direct and indirect band gap energy of titanium dioxide films deposited on glass substrate at different substrate temperatures has been listed in table 1.

Table 1. Band gap energy of titanium dioxide films deposited on glass substrate at different substrate temperatures

Substrate Temperature (°C)	Indirect Band Gap (eV)	Direct band Gap (eV)
300	3.40	3.90
350	3.45	3.93
400	3.47	3.97

CONCLUSION

The anatase phase titanium dioxide thin films have been produced by spray pyrolysis technique on glass substrates at different substrate temperatures. The crystallization is found to increase slightly with increase in substrate temperature from 300 to 400 ^{0}C. XRD patterns also support the slow growth of crystallite sizes for so obtained films. It is observed that both the allowed direct and indirect optical band gap of the films increases with the increase in substrate temperature.

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