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Effect of temperature on structural, optical and electrical properties of spray deposited TiO_2 thin films

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ABSTRACT

In present paper, the effect of the deposition temperature on structural, Optical and Electrical properties of pure TiO_2 thin films was investigated. The pure TiO_2 thin films were successfully deposited by spraying 0.1M titanium trichloride solution onto the glass substrate. The X ray diffractometric studies revealed that the deposited TiO_2 thin films have polycrystalline anatase phase with dominant (101) plane. The crystallite size was found to increase with increased substrate deposition temperature. The micro-strain and dislocation density in the film was observed to decrease as the crystallite size increased. The band gap energy of TiO_2 films with different deposition temperatures was measured using absorption spectra of UV-Vis spectrophotometer. The optical band gap of the TiO_2 films decreased from 3.30 eV to 3.54 eV as the substrate temperature was varied from 350^0C to 500^0C. The electrical resistances, temperature coefficient of resistance and activation energy of the films were calculated by measuring DC sheet resistance of the films at different temperatures.

Keywords: TiO_2 thin films, Spray pyrolysis technique, Structural, optical properties etc.

INTRODUCTION

The development of modern society considerably depends on the research in basic sciences which underline advancement in technology. During last several decades, nanotechnology has been developed dynamically; wherein nanomaterials different geometrical shapes like nano rod, flowers, belts, web like etc [1-5] were obtained to enhance their properties, such as structural, electrical, optical, photocatalytic activity, gas sensing etc. Thin film technology studies have directly or indirectly advanced many more new areas of research in solid-state Physics and Chemistry. The application areas of nanotechnology are based on the phenomena that are the unique characteristics of the thickness, geometry, surface to volume ratio, porosity and structural morphology of the films. Many new technologies have been emerged from the nanotechnology; a few to name include, etching, lithography, coating technology etc. The coating technologies have given considerable attention, mainly due to their functional advantages over bulk materials, processing flexibility, and cost considerations [6]. There are several physical and chemical methods used for film coatings. Spray pyrolysis is one of the chemical methods in which liquid precursor solution is sprayed over a substrate for a film deposition. The spray pyrolysis technique was first introduced by Chamberlin and Skarman [7] in 1966; with successful deposition of CdS thin films for solar cell applications. In general the spray pyrolysis is a simple technique with numerous advantages over the other techniques. Advantages of the method include lower cost, coating on different substrates with complex geometries, uniform and high quality coatings, ambient operations, mass production, reproducibility of films and rapid film growth rates (up to 100 nm/s) [8–12]. Titanium dioxide is one of the best candidates for solar cell application which in turn has attracted immense interest in synthesis to modify the TiO_2 nanomaterials using different techniques. Titanium dioxide exists in nature in either anatase (tetragonal, a = 3.7842 Å, c = 9.5146 Å), rutile (tetragonal, a = 4.5845, c = 2.9533 Å) or brookite (orthorhombic, a = 9.184 Å, b = 5.447 Å, c = 5.145 Å) forms[13]. Out of these, rutile is the thermodynamically stable form of titanium dioxide whereas the anatase phase rapidly transforms to rutile above 700^{o}C.In this article, influence of deposition temperature on the structural, electrical and optical properties of the titanium dioxide thin films, deposited by modified spray pyrolysis technique is reported.

METHODOLOGY

A modified spray pyrolysis setup has been developed, designed and assembled in our laboratory to overcome limitations of conventionally designed setup; such as number of optimized parameters, reliability and homogeneity of the deposited films etc. The titanium dioxide (TiO_2) thin films were deposited onto glass substrates using spray pyrolysis technique. A 0.1M precursor solution was prepared by dissolving 1m□ of titanium trichloride ($TiCl_3$) in to 77.3m□ of double distilled water. The prepared precursor solution was sprayed onto the substrate at 350^{0}C, 400^{0}C, 450 ^{0}C and 500^{0}C temperatures. The other optimized spray parameters include; Solution Flow rate= 1m□/minute, Carrier air flow rate = 7.5 □pm, Gun to substrate distance = 30cm, Solution spread = 20m□□and Spray time =20min. The deposited films were annealed in air atmosphere at 500^{0}C for 4 hr for further oxidization and crystallization. The surface properties such as the phase and crystallinity of the films were analyzed by X ray diffractmetry (XRD) using a BRUKER D8 ADVANCE diffractometer and surface morphology was studied using scanning electron microscopy (SEM) with a JEOL-540LV microscope. The electrical properties like DC sheet resistance, temperature coefficient of resistance (TCR), activation energy were characterized by static gas sensing system. The optical absorption, transmittance of deposited films was investigated using a Perkin Elmer Lambda 950 spectrophotometer (Waltham, Massachusetts, USA) in the range of 200–800 nm UV–Vis spectrometer.

RESULTS AND DISCUSSION

X Ray Diffractometry

The effect of the deposition temperature on the crystallite plane orientation of the films was investigated by calculating the texture coefficient. The texture coefficient for all the crystallite planes was calculated using the following expression. [14]

$$T_c(\mathrm{hkl}) = \frac{I(hkl)/I_0(hkl)}{(1/N)\sum I(hkl)\Big/I_0(hkl)} \quad \text{----------(1)}$$

Where $T_c(hkl)$is texture coefficient of the (hkl) plane, I(*hkl*) is the measured intensity from the (hkl) plane, $I_0(hkl)$ is JCPDS standard intensity of the (*hkl*) plane, and N is the number of diffraction peaks.

The crystallite size is evaluated using the Scherrer's formula from the average crystallite size of the all matched planes. [15].

$$D = \frac{K\lambda}{\beta\cos\theta}$$

Where K = 0.9 is the shape factor, λ is the X-ray wavelength of CuKα radiation (1.5406 Å), θ is the Bragg's angle and β is full width at half maximum of the peak.

The micro strain (ε) developed in the TiO_2 thin films can be calculated using the relation [16].

$$\varepsilon = \frac{1}{2}\left(\beta - \lambda/D\mathrm{Cos}\theta\right)\frac{1}{\tan\theta}$$

The value of dislocation density (δ) is calculated using the following relation [17]

$$\delta = n/D^2$$

Where, n is a factor, which when equal unity giving minimum dislocation density and D is the crystallite size.

X ray diffractograms of the films are given in figure 1. Films deposited at lower temperature, that is, below 300°C, show amorphous nature of [18,19]. As the deposition temperature is increased from 350°C to 500°C, the deposited films showed were polycrystalline nature with anatase TiO_2 crystalline phase. With the increase in deposition temperature, the films showed increased crystallinity, which is manifested by corresponding increase in intensity of the peaks in diffractograms. The films annealed at a temperature of 500°C were polycrystalline in nature and oriented along anatase TiO_2 (101), (112), (200), (105), (211), (204) (220), and (216) planes with the anatase plane A (101) being the predominant peak. The *as deposited* and annealed films exhibited tetragonal crystal structure with space group I41/amd, unit cell parameters a = 3.7852 Å, c = 9.5139 Å. The peak intensities showed a good agreement with the JCPDS data (#21-1272). Intensity and full-width half maximum of the diffraction peaks was observed to increase proportionally with the deposition temperature, which is in agreement with the literature. [5].

The structural parameters such as crystalline size, dislocation density and micro strain were determined from the appropriate equations and are reported in Table 1. With increasing substrate temperature, the size of the crystallites also showed an increase from 32.93 nm to 55.34 nm and is consistent with earlier reports [20]. From the table 1, it can be perceived that the strain and dislocation density in the film decreases as the crystallite size increases; which is a well-known phenomenon [21].

Scanning Electron Microscopy

The surface micrographs of TiO_2 thin films prepared at different deposition temperature and annealed at 500 °C are presented in figure 2. It is a observed from fig. that all films prepared at low temperatures i.e up to 400°C are free from the pinholes and shows formation of uniform and dense interconnected web-like structure. With increase in deposition temperature the surface roughness increases and some pinholes are appeared. Similar web-like morphology has been reported for TiO_2 thin film prepared by spray pyrolysis method [5]. The interconnected webs are of variable diameter, which may be due to the sequential growth of webs; one above another during the growth process.

Optical Properties

The optical absorption spectra of pure TiO_2 thin films deposited on glass substrate using modified spray pyrolysis technique were obtained using UV-Vis spectrophotometer. Figure 4shows the optical absorption spectra of pure TiO_2 thin films deposited at 350°C and 500°C. The absorption edge was found to be sharp and showed a shift towards lower wavelength region with increase in the deposition temperature. This may be due to the change in crystal orientation in the film. The optical absorption spectra of TiO_2 films were investigated in the wavelength range 200-900 nm, at ambient temperature. The energy band gap of the films was evaluated from the relation [22] $(\alpha h\nu)^2 = A(h\nu - E_g)$

Where A is a proportionality constant and E_g is the direct transition band gap, α is optical absorption coefficient as a function of the wavelength; estimated using the relation from the $(\alpha h\nu)^2$ Vs h□ plot, as shown in figure 3. The band gap values decreased from 3.54 eV to 3.30 eV with increase in substrate temperature as shown in table 1. This may be due to the increase in grain size corresponding increase in deposition temperature and is consistent with quantum confinement effect [23].

Electrical Properties

The electrical properties, namely, electrical resistance, temperature coefficient of resistance (TCR), and activation energy were determined using static gas sensing system. The electric resistance of the films was measured at different temperatures with the help of half bridge method. The measured electric resistance was found to decrease with increase in temperature of the films. The thermal activation energy of the films was measured from the slope of the Arrhenius plot. The temperature coefficient of resistance was estimated using the relation.

$$\alpha = \frac{1}{R_t}\left(\frac{R_2 - R_1}{T_2 - T_1}\right)$$

where R_t is resistance of the film at room temperature and $\frac{R_2 - R_1}{T_2 - T_1}$ is slope of the resistance versus temperature plot. The measured values of film resistance at room temperature, TCR and activation energy for heating and cooling cycle are presented in table 1.

Table 1: Influence of deposition temperature on structural Optical and electrical properties of TiO_2 thin film deposited using spray pyrolysis technique.

Sample	Crystallite Size (nm)	Texture coefficient of (101) plane	Micro strain	Dislocation density	Optical Band gap	TCR $(^0C^{-1})$	Activation energy (eV)
S_{350}	32.93	1.3781	0.1068	0.03036	3.54	0.0014068	0.339566
S_{400}	40.09	1.5239	0.08769	0.02494	3.48	0.0010697	0.326715
S_{450}	53.08	1.4791	0.06644	0.01883	3.39	0.0010115	0.313691
S_{500}	55.34	1.3821	0.06346	0.01807	3.30	0.001004	0.299029

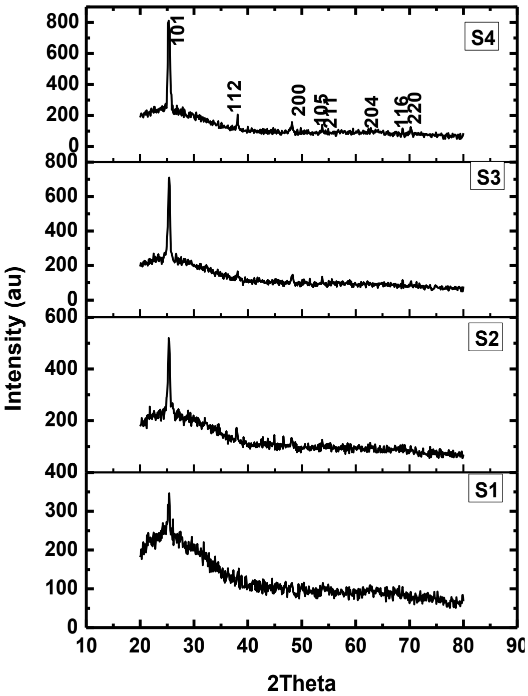

Figure 1: XRD spectra of TiO_2 thin films deposited at different substrate temperature.

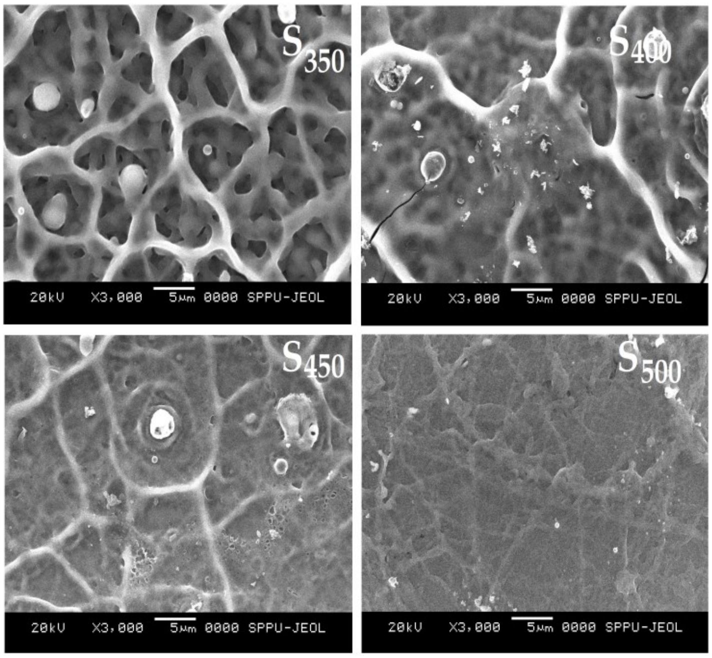

Figure 2: SEM images of spray pyrolysis deposited TiO_2 thin films for different deposition temperature from 350 ^0C to 500 ^0C.

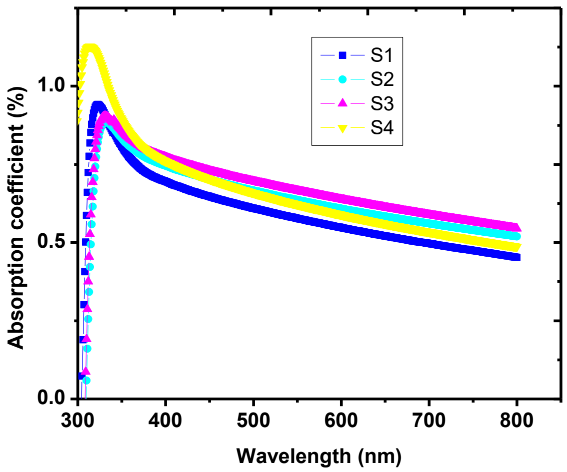

Figure 3: Optical absorption spectra of TiO_2 thin films for different deposition temperature.

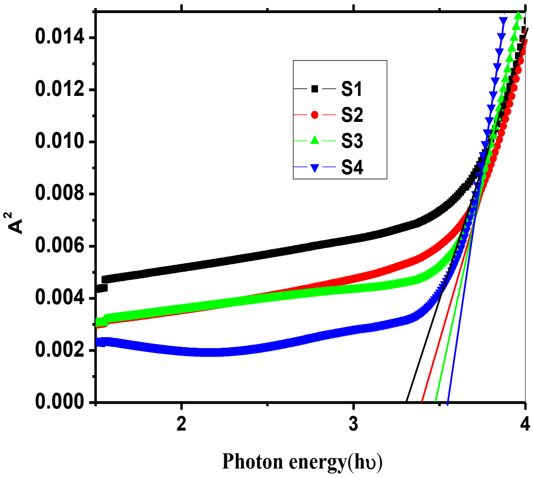

Figure 4: optical band gap calculations.

The temperature coefficient of resistance and activation energy of the films was found to decrease with increase in film deposition temperature [24]. As the deposition temperature increases the thickness of the film decreases therefore, the activation energy of the film also showed a declining nature.

CONCLUSION

The pure TiO_2 thin films were successfully deposited by spraying 0.1M titanium trichloride solution onto the glass substrate. The XRD study revealed that the deposited TiO_2 thin films have polycrystalline anatase phase with dominant (101) plane. The crystallite size of the film material was found to increase with increased deposition (substrate) temperature. The micro-strain and dislocation density of the films were decreased with increase in crystallite size. The optical band gap of the TiO_2 films was observed to decrease from 3.54 eV to 3.30 eV as the deposition temperature was increased from 350^{0}C to 500^{0}C. The temperature coefficient of resistance and activation energy of the films showed inverse variation with deposition temperature. The electrical resistance of the films decreased with temperature of film, which reveals semiconducting nature of the film material.

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