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Preparation and Characterization of Nanocrystalline TiO2 Thin Films Prepared By Sol-Gel Spin Coating Method

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ABSTRACT: Titanium dioxide(TiO_2)thin films were synthesized via sol-gel spin coating method using titanium tetra isopropoxide (TTIP) as starting material. TTIP is dissolved in ethanol stabilized by glacial acetic acid. TiO_2 thin films were prepared for different proportions of acetic acid. The prepared samples were dried at 250°C for 5minutes then annealed at 500°C for 1hr. The structural properties were investigated by using X-ray diffraction technique and grain size was calculated. Elemental analysis and surface morphology were studied using EDX spectrum and SEM micrograph. Absorbance spectra were measured by using UV-Vis spectrophotometer and the optical band gap was calculated. The crystalline size of TiO_2 thin films obtained is ~19.67nm.

KEYWORDS: TiO_2 thin films, Sol-gel, Anatase.

I. INTRODUCTION

Titanium-di-oxide isthe most attracted materials in nano science and nano technology because of having a lot of interesting properties from fundamental and practical point of view [1]. Crystalline titania has three modification phases which are rutile(tetragonal) [2]anatase(tetragonal) and brookite (orthoromphic)[3]. Titania nano particles have received much interest for applications such as optical devices, sensors, and solar cell applications . There are several factors in determining important properties in the performance of TiO_2 for applications such as particle size, crystallinity and the morphology[4-6].Many methods have been established for titania synthesis such as sol-gel technique [5], hydrothermal method [6],chemical vapour deposition [7,8], direct oxidation method and others[10]. Among them sol-gel technique is one of the most used method due to its possibility of deriving unique metastable structure at low reaction temperatures and excellent chemical homogeneity [11]. In this work we report novel sol-gel spin coated TiO_2 thin film were prepared and the prepared thin films were analyzed.

Photovoltaic cells containing organic semiconductors have attracted considerable attention[11][12][13] because of their electrical and optical properties can be varied widely, and generally they can be fabricated more easily than inorganic photovoltaic cells. The randomly porous structure of the TiO_2 electrode gives raise to several undesirable characteristics. These include a low conductivity, which is due to the fact that the film consists of tiny crystals measuring 10-30nm in diameter [14]. The small size of the crystals does not support the formation of a space charge region. This has to enhance the recombination rate of the photo-injected electrons due to the absence of an energy barrier at the electrode/electrolyte interface.

Sol-gel processing of titanium dioxide has been extensively investigated, and modern processes have been developed to refine and control the stability, as well as the phase formation of the colloidal precursor[15]. The hydrolysis of the titanium tetra isopropoxide combined with acetic acid and ethanol with subsequent annealing has led to new materials characterized by their controlled porosity and strong adhesion to the substrate[16].

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II. MATERIALS AND METHODS

2.1 Preparation of TiO_2 sol:

Titanium tetra isopropoxide ($C_{12}H_{28}O_4Ti$), Acetic acid ($C_2H_4O_2$) and Ethanol (C_2H_5OH) were used to prepare the coating solution. All chemicals were of analytical grade and were used without further purification. The precursor (TTIP) was added with the solvent (ethanol) and acetic acid was added with above solution. Stirring process was performed for about four to five hours. Different combinations of TiO_2 sol were prepared by altering the concentration of acetic acid in the ratio of TTIP: CH_3COOH:C_2H_5OH shown in table 1.

Table:1 Chemical composition used for prepared TiO_2 thin films

SAMPLES	TTIP(ml)	ACETIC ACID (ml)	ETHANOL (ml)
X	1.5	0.1	10
Y	1.5	0.2	10
Z	1.5	0.3	10

2.2 Preparation of thin films

The TiO_2thin films were prepared on glass substrates. The solution was dropped on the well cleaned glass substrates and the substrates were allowed to rotate at 3000 rpm for 45s. After each coating TiO_2 films were dried at 100^oC for 10 min. The spin-coating and drying process were repeated for ten times. The prepare film annealed at 500^oC for two hours. The flow chart of preparation of Tio_2 nano crystalline thin films given in Fig 1.

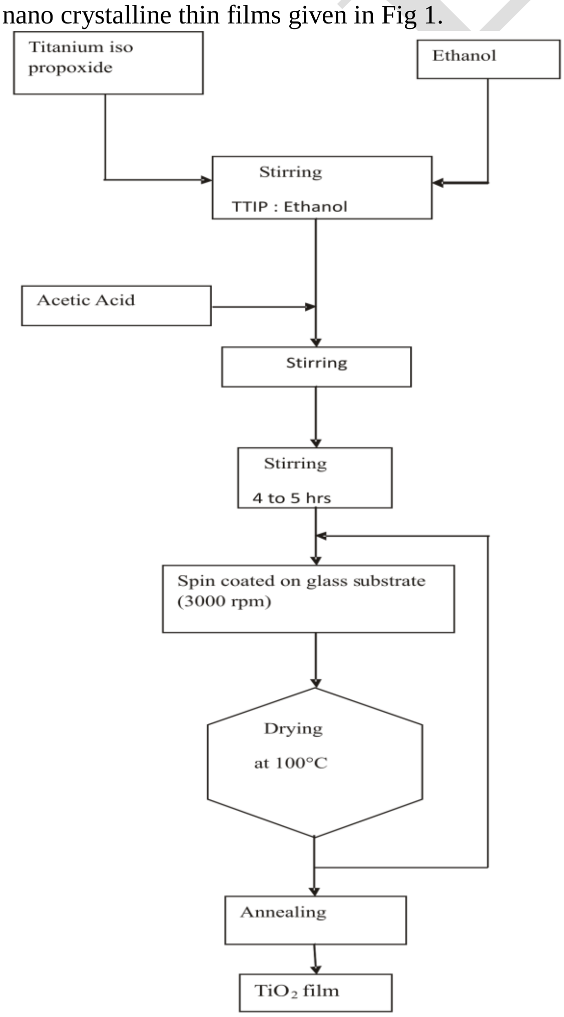

Fig 1: Flow chart depicting the preparation of TiO_2 thin films.

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2.3 Characterization of TiO_2thin films

The crystallinity of each TiO_2 film was determined by X-ray diffraction using an (XPERT-PRO) X-ray diffract meter witu CuK_α radiation source in the range of 20-70^o. Elemental compositions and surface morphological analysis of the prepared samples have been studied using scanning electron microscope (Hitachi VP-SEM S-3400N). The optical properties were studied by using a UV-Visible spectrophotometer (JASCO Corp., V-570).

III. RESULTS AND DISCUSSION

Fig 2 shows the x-ray diffraction pattern of the TiO_2 thin films prepared using different acetic acid concentrations (0.1,0.2 and 0.3ml) and annealed at 500°C.All the prepared films shows both rutile and anatase phase. Increase in the actic acid concentration results in change in intensity of the peak improves crystllinity.

The crystal size was calculated by the strongest peaks of TiO_2 corresponding to anatase(101). The mean crystal size 'd' was determined from the broadening β of the most intense line , for each polymorph in the x-ray diffraction pattern based on the Scherrer's equation

$$D=K\lambda/\beta\cos\theta$$

λ- radiation wavelength
k- 0.90
θ- Bragg angle.

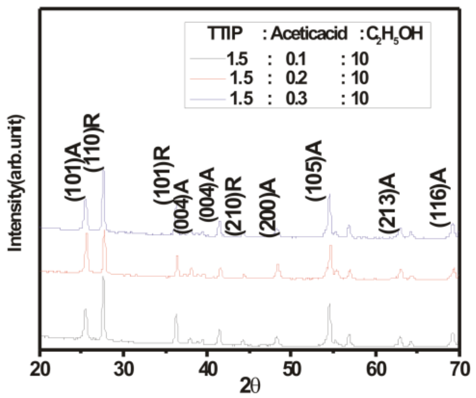

Fig 2: XRD patterns of the sol-gel spin coated nano crystalline TiO_2 thin films

It is evident that the anatase peak become rutile peaks with increasing catalyst concentration and that diffraction pattern displays the coexistence of both amorphous and crystalline TiO_2 regions showing the simultaneous presence of the broad hump in the low 2θ region demonstrating short range order and amorphicity. The diffraction pattern of film with strongest peak shows the formation of phase pure anatase TiO_2 thin film crystallites. It should be noted that for all three acetic acid concentrations produces strong peaks exactly at 25.3°. The crystallite size of anatase phase , used as a measure of TiO_2 crystallinity decreased with increasing the proportion of the acetic acid(grain size≈27 to 13nm). It is suggested that the increase in surface area and porocity of the TiO_2 anatase phase is mainly because of varying the concentration of acetic acid.

The matching of the observed and standard 'd ' values conforms that the deposited films are of phase-pure anatase TiO_2 with tetragonal structure. The strongest peaks for film deposited for various properties of solvent and stabilizer the estimated grain size,27.55nm, 18.35nm and 13.15nm(annealed at 600°c) reveals decrease in grain size with increase of acetic acid concentraction.

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SEM CHARACTERIZATION

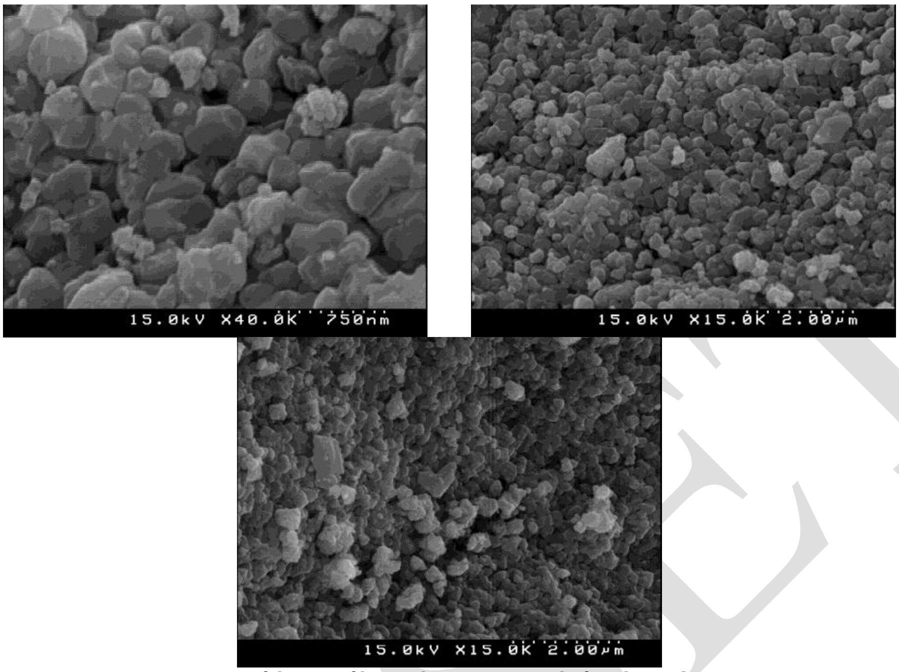

Fig.3: SEM images of the TiO_2 films with 0.1, 0.2, 0.3 ml of acidic acid concentrations

The Figure 3 shows the SEM image of the TiO_2 thin films at various acetic acid concentrations. The particle size decreases as the acetic acid concentration increases. This SEM result reveals that the catalyst concentration affects grain size and confirms the result obtained from XRD.

UV VIS CHARACTERISTICS

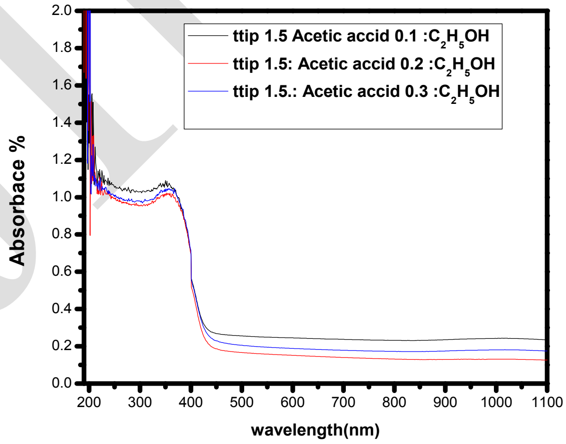

Fig 4: UV-Vis absorbance spectra and band gap of nano crystalline TiO_2 thin films

The UV absorbance spectram of TiO_2 thin film prepared for various acetic acid concentration shown in fig.4. The optical absorbance spectra of TiO_2 thin films samples exhibit strong absorption below 400nm. The direct band gap (E_g) of the sample is determined by fitting the absorption data to the direct transition

$$\alpha h\nu = E_d\,(h\nu - E_g)^{1/2}$$

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where α is the optical absorption coefficient, hν is the photon energy, E_g is the direct band gap, and E_d is a constant. The band gap range of 3.0eV obtained by 0.1, 0.2 and 0.3 ml concentration is in accordance with the band gap of reported anatase phase.

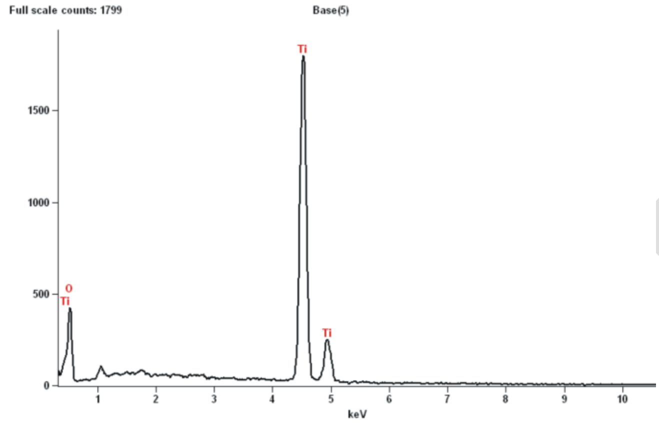

Figure 5. Energy dispersive X-ray spectrometry (EDAX) of nano crystalline TiO_2 thin films.

Energy dispersive X-ray spectrometry (EDAX) analysis of TiO_2 thin films at 600°c shows peaks for Ti element and oxygen. There is no trace of any other impurities could be seen within the detection limit of the EDAX as presented in figure 5.

IV. COCLUSION

TiO_2 thin films have been prepared by sol-gel route using titanium tetra isopropoxide. By controlling the acetic acid concentration TiO_2 thin films with the grain size of approximately13.15 to 27.55nm have been obtained. The surface morphological studies obtained from SEM micrograph showed that the particles with the spherical shape. The typical composition of TiO_2 thin films under various catalyst concentration was investigated. The X-ray diffraction result clearly shows that the crystal size decreased with increase in acetic acid concentration.

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