INTRODUCTION

Thin film of Titanium dioxide (TiO₂) has generated a lot of interest because of its attractive properties such as wide band gap (Young Ran park, et al., 2005), high refractive index (Kasikow, et al., 2006) high dielectric constant (Ulrike, et al., 2003) and absence of non-toxicity. TiO₂ thin films have been widely investigated for various optical applications and have attracted considerable attention for optical filter, gas sensor, ceramic membranes, photocatalysts and solar cells. Three crystallographic modifications occur in TiO₂: Brookitite, Anatase and Rutile. The anatase phase has formed when at growth temperature between 400 – 700°C and then after 700°C the rutile was formed. The rutile phase has greater density (ρ=4.25 g/cm³) and refractive index (n=2.75 at λ=550 nm) than the anatase phase (ρ = 3.89 g/cm³ and n=2.54 at λ=550 nm). A film formation of TiO₂ can be carried out by various methods such as sol-gel, spray pyrolysis, sputtering, pulsed laser deposition and electrodeposition. Among these techniques, spray pyrolysis is a simple, cost-effective technique for large area deposition and also excellent method for the deposition of metallic oxides thin films. The present study is focused on structural and optical properties of titanium dioxide thin films prepared by microcontroller based spray pyrolysis technique using precursor solution of Titanium acetylacetonate have been investigated.

MATERIALS AND METHODS

The TiO₂ films were deposited on microscopic glass substrates using spray pyrolysis technique. The experimental technique has been previously described. For deposition, 0.1 M of Ti(acac) was dissolved in ethanol and sprayed onto microscopic glass substrates with dimensions of 75x25 mm² at different substrate temperatures (T=375, 400, 425 and 450°C) and annealed at 500°C for 1h in air. The substrates were first cleaned with water bath, followed by dipping in con.HCl, acetone and ethanol successively. Finally the substrates were rinsed in deionised water and allowed to dry in a hot air oven. The values of optimized parameters are given below.

- Spray time : 15 minutes
- Solution flow rate : 3 ml/min
- Air flow rate : 1 kg/cm²
- Spray nozzle to substrate distance: 20 cm

After the deposition, the films were allowed to cool slowly to room temperature and washed with deionized water and then dried.

The structural characterization of the deposited films were carried out by X-ray diffraction technique on JEOL JDX - 803 g diffractometer (monochromatic CuKα radiation, λ=1.5406 A). The XRD patterns were recorded in 2θ interval from 10° to 80° with the steps of 0.05° at room temperature. The surface morphology was studied by using SEM (JEOL-JES-1600) with a magnification of 10K. Optical absorption spectrum was recorded in the range 350-900 nm using Varian-Cary 500 scan double-beam spectrophotometer.

RESULTS AND DISCUSSION

The XRD profiles of TiO₂ films deposited at different substrate temperatures and annealed at 500°C for 1h are shown in Fig.1. The annealed film is polycrystalline in nature and oriented along A (101) and A (200) planes, A (101) being the predominant peak. The films exhibited tetragonal crystal structure and the peak intensities are in agreement with the JCPDS data (No. 21-1272). The intensity of the diffraction peaks gradually increases and full-width half maximum value increases with increase in substrate temperature and the observed peaks are in agreement with the reported value. The crystallite size is evaluated from the FWHM of the (101) plane using the Scherrer’s formula:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

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where $K=0.94$ is the shape factor, $\lambda$ is the X-ray wavelength of CuKα radiation, $\theta$ is the Bragg’s angle and $\beta$ is the full width at half maximum of the peaks. The micro strain ($\varepsilon$) is calculated using the relation

$$\varepsilon = \frac{\beta \cos \theta}{4}$$

The value of dislocation density ($\delta$) is calculated using the relation

$$\delta = \frac{1}{D^2}$$

The effect of substrate temperature on the micro-structural parameters of TiO$_2$ films are summarized in table 1. From the table, the crystallite size of TiO$_2$ thin films can be tuned between 42 to 25 nm by varying the substrate temperature. It is observed that strain and dislocation density increases as there is decrease in the crystallite size. Micrograph well surface smoothness and uniformity. Average grain size for the films is observed about < 0.5 µm. A representative EDS spectrum of the TiO$_2$ film deposited at 450°C is shown in Fig.3. It is found that titaniaum and oxygen are present in near stoichiometric ratio (Ti: O =20:80 at %)

The optical transmission spectra of TiO$_2$ films are measured in the wavelength range 350-900 nm at room temperature. The energy band gap of the film is evaluated from the relation

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where $A$ is a proportionality constant and $E_g$ is the direct transition band gap. From the $(\alpha h\nu)^2$ vs $h\nu$ plot, shown in Fig.6. The band gap values decreased from 3.45 to 3.2 eV with increase of substrate temperature and this similar behavior was also observed earlier (Mechiakh, et al., 2011). The refractive index is calculated using the relation

$$n = \frac{1+R^{4/2}}{1-R^{4/2}}$$

where $R$ is the optical reflectance. Fig.5 shows the variation of refractive index with different wavelengths of the TiO$_2$ films. From the result, it shows that there is increase in the refractive index in the UV region and the values are decreased gradually from 2.6 to 2.1 in the high transmission range.

**Figure 1** XRD spectra for the annealed TiO$_2$ films obtained at different substrate temperatures

**Figure 2** SEM images for the annealed TiO$_2$ films prepared at $T_s$=450°C

**Figure 3** EDS spectrum for the annealed TiO$_2$ film prepared at $T_s$=450°C

**Figure 4** $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ for the annealed TiO$_2$ films grown at (a) $T_s$=375°C, (b) $T_s$=400°C, (c) $T_s$=425°C, (d) $T_s$=450°C

**Figure 5** Variation of refractive index (n) versus wavelength for the annealed TiO$_2$ films grown at (a) $T_s$=375°C, (b) $T_s$=400°C, (c) $T_s$=425°C, (d) $T_s$=450°C
CONCLUSION

TiO$_2$ thin films have been deposited on glass substrate by spray pyrolysis technique at different substrate temperature and annealed at 500°C for 1h in air. The XRD pattern revealed that the films are polycrystalline in nature along with (101) plane of anatase tetragonal structure. The crystallite size is decreased from 42 to 25 nm and the band gap value decreased from 3.45 to 3.2 eV as the substrate temperature increases.

The refractive index and extinction coefficient values are also calculated. The properties of TiO$_2$ thin films are suitable for fabricating the opto-electronic devices.

**References**


<table>
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<tr>
<th>Substrate temperature (ºC)</th>
<th>Crystallite Size (nm)</th>
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Table 1 Micro-structural parameters for the annealed TiO$_2$ films obtained at different substrate temperatures.