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EFFECT OF ANNEALING TEMPERATURE ON STRUCTURAL AND OPTICAL PROPERTIES OF SiO_2 DOPED TiO_2 THIN FILMS PREPARED BY SOL GEL METHOD

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ABSTRACT

SiO_2 - TiO_2 thin films were deposited on glass substrates using dip coating technique. The preparedSiO_2 - TiO_2thin films were annealed at 300°C,400°C and 500°C respectively. Characterization was done using X – ray diffractometry [XRD], UV visible spectroscopy [UV Vis], Photoluminescence spectroscopy [PL] and Scanning Electron Microscopy [SEM]. As the annealing temperature increased, the crystallite size of the SiO_2 - TiO_2 was also increased. The SEM investigations show that the films are having fractured morphology. The UV analysis reveals that optical band gap energy decreases as the temperature is increased. The results showed that the structural and optical properties of SiO_2 - TiO_2 could be affected by changing the annealing temperature.

Keywords: SiO_2 - TiO_2 thin films, dip coating method, XRD, SEM, UV

I. INTRODUCTION

Titanium dioxide thin films are extensively studied because of their interesting chemical, electrical and optical properties, high refractive index, high dielectric constant and ability to be easily doped with active ions which are considered for various applications such as gas sensors [1], planar waveguides [2], electro chromic systems [3] and photo catalysts [4].

Addition of another semi conductor has been used to improve the physical properties of titanium dioxide. In principle, the coupling of different semiconductor oxides seems useful in order to achieve a higher photocatalytic activity [5]. Various composites formed by TiO_2 and other inorganic oxides such as SiO_2 [6], ZrO_2 [7], SnO_2 [8], Cu_2O[9] and MgO [10] have been reported. SiO_2 doped TiO_2 enlarges surface area and visible light photoactivity of TiO_2[11]. Nano crystalline SiO_2-TiO_2 can be prepared using Physical Vapour Deposition (PVD) [12], Plasma Enhanced Chemicals Vapour Deposition [PECVD][13], Metal Organic Decomposition[MOD][14] and sol-gel process [15]. Out of this sol-gel process Dip coating process has more advantages like low cost, excellent control on the film purity, homogeneity, simultaneous coating of two faces and possibility of forming multi and mixed layers.

The aim of this work is to prepare and study the influence of annealing temperature on structural and optical properties of the SiO_2 - TiO_2 thin films on glass substrate.

II. EXPERIMENTAL DETAILS

Preparation of the films

SiO_2 - TiO_2 thin films were deposited on optical transparent microscopy glass slides [75 x 25 x 2 mm]. The substrates were carefully precleaned prior to coating. A dip coating apparatus was used for the deposition. The substrates were immersed into the coating solution and then withdrawn at a regulated speed of 50 mm/30 s.

The SiO_2 - TiO_2 precursor sol was prepared by mixing 4 ml of Titanium Tetra Iso Propoxide [TTIP], 30 ml of ethanol, 1 ml of acetic acid and 1 mol percent of Tetra Ethyl Ortho Silicate [TEOS]. The solution was stirred for an hour. Then glass substrates were immersed in this sol, withdrawn and then dried at 100°C for 10 minute. This procedure was repeated several times to obtain samples with increasing thickness. Finally the thin films were heat treated in the temperature range 300°C - 500°C for 3hours in the furnace.

To examine the crystal structure of SiO_2-TiO_2 thin films, X' pert pro diffractometer with C_uk_α radiation [k = 0.154nm] in steps of 0.1 over the 2θ range of 20° – 80° was utilized to determine the crystallization degree of the thin films. UV–Visible spectra were recorded by using the (Schimadzu 1800) UV–VIS–NIR spectrometer. The photoluminescence (PL) spectra of prepared thin films were recorded using (Schimadzu RF–5301) photoluminescence spectrometer with xenon lamp as the light source at room temperature at an excitation wavelength of 410 nm. The surface morphology and elemental analysis of the thin films were observed by [Hitachi S-3000H] scanning electron microscopy [SEM] and (Bruker) EDAX respectively.

III. RESULTS AND DISCUSSION

Influence of temperature on the crystallization of SiO_2 - TiO_2 thin films

The prepared SiO_2 - TiO_2 thin films were annealed under atmospheric pressure at various temperatures. Figure1 illustrates that the XRD patterns of SiO_2 - TiO_2 thin films annealed under atmospheric pressure at different temperatures in the range 300°C - 500°C for 3hours. With 300°C annealing, no diffraction peaks were detected in the XRD pattern indicating that the film remained amorphous nature.

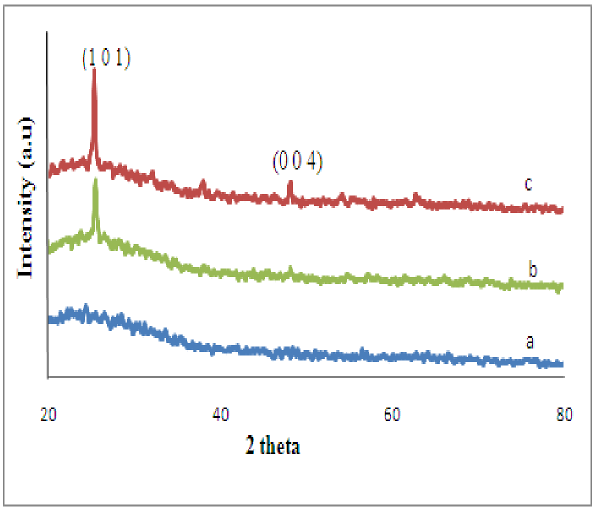


Fig. 1 XRD pattern of SiO_2 -TiO_2 thin films annealed at (a) 300°C (b) 400°C (c) 500°C

When the film was annealed at 400°C, mono phasic anatase type film was formed as indicated in the corresponding XRD pattern in which all diffraction peaks are consistent with the JCPDS data [File no.89 - 4203]. With a further increasing in the annealing temperature, the diffraction peaks became sharpened and their Full Width Half Maximum [FWHM] became narrower, revealing that the crystallinity of the annealed films is enhanced with high-temperature annealing. As the annealing temperature reached 500°C, well-crystallized anatase phase of SiO_2-TiO_2 film was obtained.

The crystallite size of SiO_2 - TiO_2 thin films were calculated by using Scherer's formula.

$$D = \frac{k\lambda}{\beta Cos\theta}(nm) \quad (1)$$

β is the FWHM in radians , θ is the Bragg's angle and λ is the X-ray wavelength [C_uk_α = 0.15405 nm].

Using the crystallite size D, the dislocation density (δ), and the strain (ε) in the films has been determined.

$$\delta = \frac{1}{D^2} \quad \text{lines / m}^2 \quad (2)$$

$$\varepsilon = \frac{\beta\ Cos\theta}{4} \quad (3)$$

The calculated structural parameters are presented in Table 1. From Table 1, it was observed that, the crystallite size increases from 53.9 nm to 59.2 nm as the annealing temperature increases. The dislocation density and microstrain decreases as the annealing temperature increases. This may be due to the improvement in crystallinity of the films with increase in annealing temperature.

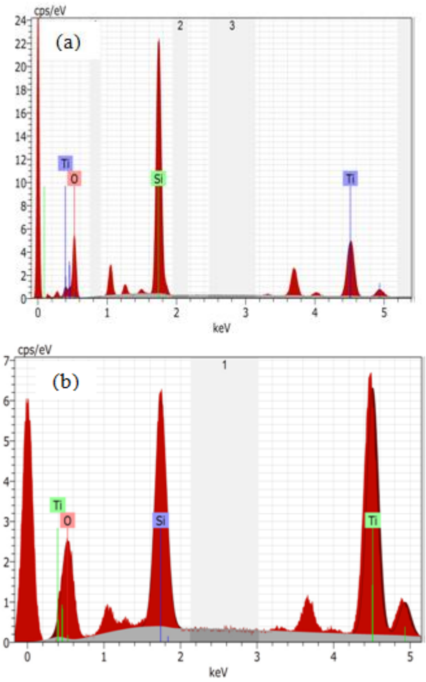
Similar results have been shown by earlier literature Rathinamala et al., [16].

Table 1: Structural Parameters of SiO_2 - TiO_2 thin film

Annealing Temperature	Crystallite size D (nm)	Dislocation Density δx 10^{14}lines/m^2	Microstrain ε
300°C	-	-	-
400°C	53.9	3.43	.04
500°C	59.2	2.8	.03

Scanning Electron Microscopy and EDX

The elemental composition of films is further identified by EDX measurement. EDX results shown in Figure 2 (a), 2 (b), 2 (c) demonstrate the peaks of Ti, O and Si can be clearly seen in the survey spectrum of SiO_2 - TiO_2 thin films for three different annealing temperature.



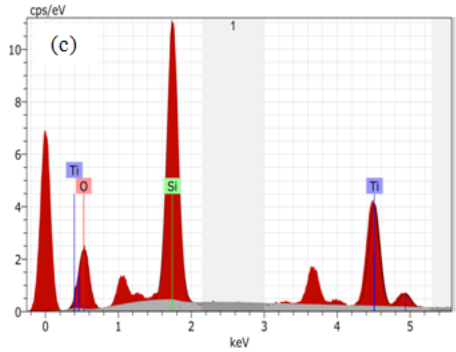
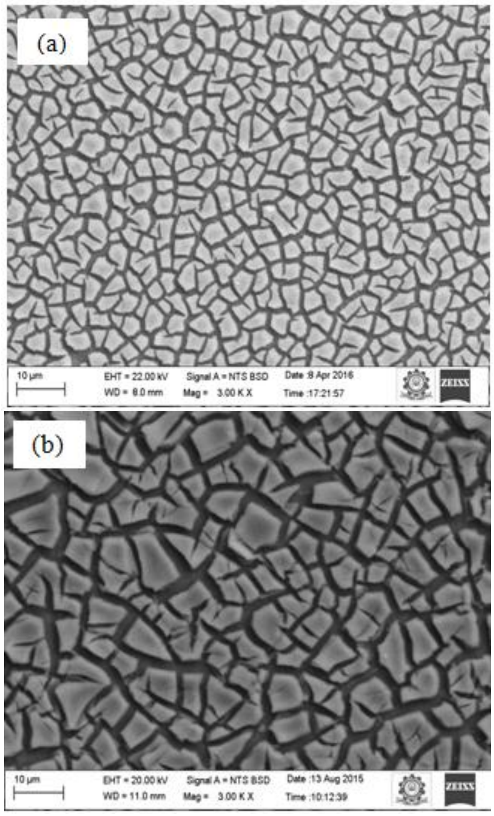


Fig. 2 EDX spectra of SiO_2 -TiO_2 thin films annealed at
(a) 300°C (b) 400°C (c) 500°C

The SiO_2 - TiO_2 thin films were observed in a Scanning Electron Microscope [SEM] to investigate their structure and surface characteristics. Microstructure of the samples after being annealed at different temperatures is shown in Figure 3. Thin films produced by this technique indicate fractured morphology. During the drying and annealing process of the films, crack formation takes place as a result of contraction stress and different thermal coefficient of expansion of the over layer and substrate [17].



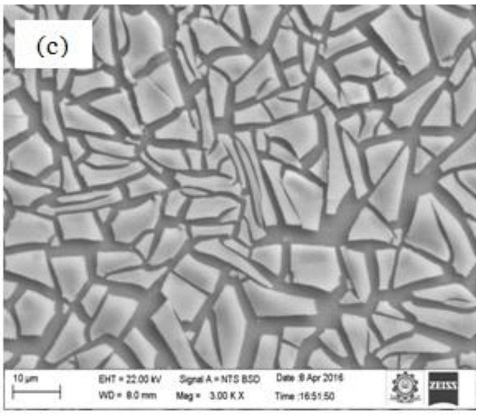


Fig. 3SEM images of SiO_2 -TiO_2 thin films annealed at
(a) 300°C (b) 400°C (c) 500°C

Optical analysis

The band gap energy can be estimated from the optical absorption measurements. The plot of ((αhν)^2) with photon energy (hν) is shown in Figure 4.

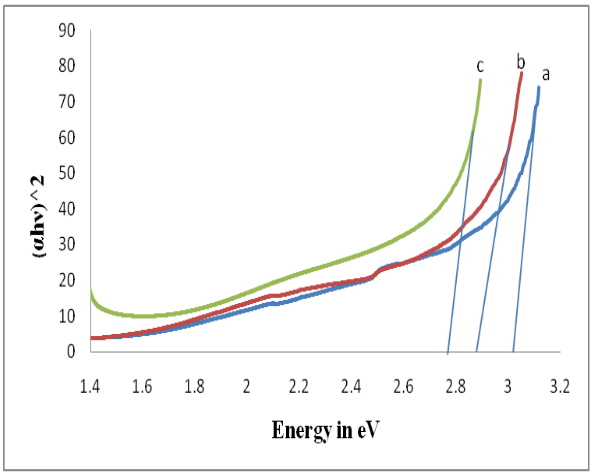


Fig. 4 Band gap of SiO_2 - TiO_2 thin films annealed at
(a) 300˚C (b) 400˚C (c) 500˚C

The band gap energy E_g can be calculated by using following equation.

$$\alpha h\nu = A(h\nu - E_g)^m \quad (4)$$

where A is a constant related to the effective masses associated with the bands and m = ½ for direct transition, α the absorption coefficient and E_g the optical band gap energy. E_g can be determined by extrapolating the straight line portion at α= 0. The band gap energy E_g of SiO_2 - TiO_2 thin films decrease owing to an increase in annealing temperature. The values are 2.9, 2.7 and 2.6 eV at 300°C, 400°C and 500°C respectively. On annealing the crystallite size increases resulting in the decrease of the band gap. The change in band gap with temperature is attributed to the quantum size effects [18].

Photoluminescence analysis

The PL spectra have been recorded at room temperature with an excitation wavelength of 410 nm. The PL emission spectra can be useful to disclose the efficiency of charge carrier trapping, immigration and transfer and to understand the fate of electrons and holes in semiconductor since PL emission results from the recombination of free carriers [19 – 21].Figure 5 shows the PL spectra of SiO_2 - TiO_2thin films annealed at 300°C, 400°C and 500°C in the range of 450 and 600 nm. Two emission peaks appear at about 485 and 560 nm wavelengths which are equivalent to the band gap of 2.6 and 2.2 eV respectively.

A possible explanation for the blue band emission at 485 nm (Figure 5) is that it is related to the confinement effects and the direct inversion of the fundamental adsorption edge for the nanometric dimension of the crystallite [22]. The other green band composed of a peak centered at around 560 nm originated from radiative recombination which was related to the grain size distribution [23]. The sample annealed at 300°C shows high emission intensity with increasing annealing temperature, there is a significant decrease in the intensity of PL spectra.

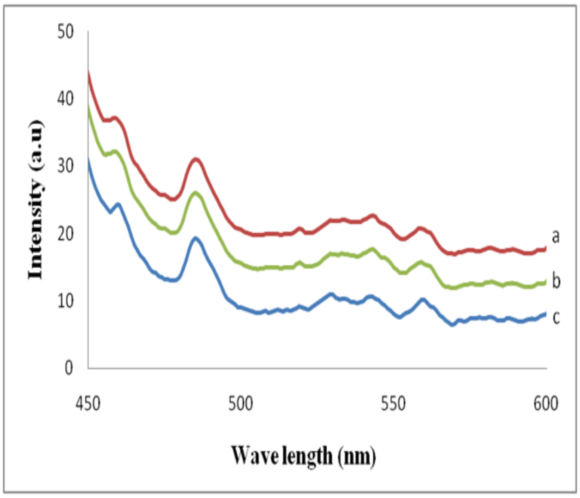


Fig. 5 PL spectra of SiO_2-TiO_2 thin films annealed at (a) 300°C (b) 400°C (c) 500°C

The PL emission mainly results from the recombination of excited electrons and holes and the lower PL intensity indicates the decrease in recombination rate [19 - 21]. At 500°C, the lowest PL intensity was observed due to the SiO_2 - TiO_2 thin film with better crystallization.

IV. CONCLUSION

SiO_2 - TiO_2 thin films have been successfully deposited onto glass substrates by the dip coating technique and annealed at different temperatures. The structural, surface morphological and optical properties of the SiO_2 - TiO_2 thin films were investigated by using SEM and XRD measurements. SEM measurements showed that the films are having fractured structure. The XRD measurements showed that the films annealed at 400°C and above exhibited anatase phase with tetragonal structure having a preferential orientation along (101) plane. Optical investigations show that there is a decrease in band gap as the annealing temperature increases. The photoluminescence spectra show that the intensity of PL emission peaks found to decrease with increase in annealing temperature. The results show that the prepared SiO_2 - TiO_2 thin films can be applicable for photocatalytic and self cleaning applications.

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