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EFFECT OF SIO_2 DOPANT ON STRUCTURAL AND OPTICAL CHARACTERIZATION OF TIO_2 THIN FILMS BY SOL-GEL METHOD

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Abstract: ***SiO_2 doped TiO_2 thin films were synthesized on glass substrates by sol-gel dip coating method. The thin films were analyzed for different concentration of SiO_2. The prepared films were preannealed at 100°C and post annealed at 400°C. The XRD pattern of the films confirmed tetragonal structure with the nanocrystalline nature. The films exhibited a pure anatase phase with a strong orientation along (101) plane. Scherrer's formula was used to calculate crystallite size. Surface morphology of films were studied using SEM. The presence of Si with Ti and O was confirmed using EDAX. The band gap energy was calculated using UV – VIS spectroscopy. The thickness results suggested that thickness of the film increases with the increase in the concentration of dopant. The room temperature PL spectra of thin films showed blue and green emissions at 485 nm and 560 nm. The surface roughness of the thin film was characterized by AFM.***

Keywords **– SiO_2:TiO_2 thin films, dip coating, XRD, SEM, EDAX, UV, PL, AFM**

I. INTRODUCTION

Transparent Conducting Oxide (TCO) materials are of great interest due to their distinctive physical, chemical, optical and opto electronic properties. Various TCO materials are ZnO, CdO, SnO, TiO_2 etc., Among these TiO_2 plays a promising role in several areas of research because of its efficient photo catalytic activity, high refractive index, resistance to photo corrosion, chemical stability, low cost and non – toxicity [1]. Another importance of TiO_2 in recent years is the specialization of self – sterilizing surfaces and their implementation in hospitals because of its reliability and stability under irradiation [2]. There are three crystalline phases of TiO_2, namely anatase, rutile and brookite. Depending on the phase structure, TiO_2 films can be tailored for different applications. So it is necessary to understand the phase structure of TiO_2. The phase transformation of TiO_2 depends on the annealing temperature and dopant [3].The phase structure and semiconducting properties of TiO_2 films can be strongly modified by doping with impurities like Ag, Fe, Cu, Zn, SiO_2 [4] etc., Additionally the presence of dopant could increase the adhesion and mechanical stability of thin film on substrates which play a key role in device reliability [5, 6]. Nano crystalline silica doped TiO_2 thin films (SiO_2:TiO_2) can be produced by several techniques such as physical vapour deposition, chemical vapour deposition, pulsed laser deposition, magnetron sputtering, sol – gel process and electro deposition. Among these, the sol – gel technique is regarded as a cost effective method for the production of films and also involves simple processing steps [7].

The present work reports on preparation of nano crystalline SiO_2:TiO_2 by sol – gel method using dip coating technique and the effect of dopant on structural, optical properties and surface morphology with elemental analysis

II. EXPERIMENTAL DETAILS

For the preparation of the target solution, Titanium Tetra Iso Propoxide (TTIP), Tetra Ethyl Ortho Silicate (TEOS), ethanol and acetic acid were obtained and used without further purification.

SiO_2:TiO_2 solution was prepared in the following method. Firstly 4ml TTIP was mixed with 30 ml of ethanol. Secondly 1ml acetic acid was added to stabilize the solution and stirred for 30 minutes. Thirdly TEOS was added to the solution in various concentrations (0.1ml, 0.2ml and 0.3ml) and stirred for one hour. SiO_2:TiO_2 composites were deposited on glass substrates by the dip coating method with a speed of 50mm/30s. The films were dried at 100° for 5 minutes. The multi layer films of 6 coatings were obtained by repeating the above procedure. Finally the films were annealed at 400°C for three hours.

III. RESULTS AND DISCUSSION

Structural Analysis

X-ray diffraction profiles of SiO_2:TiO_2 thin films annealed at 400°C for various concentration of Si is shown in Figure 1. The deposited films show nanocrystalline nature with

high intensity peak in (101) orientation having anatase phase with tetragonal BCC structure [1]. It also shows that the intensity and Full Width Half Maximum (FWHM) increased with SiO_2. The diffraction peak from the XRD pattern is in agreement with the JCPDS card no 89-4203. The crystallite size was determined from XRD peaks using the Debye – Scherrer's formula

$$D=\frac{K\lambda}{\beta\cos\theta}(nm) \qquad (1)$$

where D is the crystallite size; λ is the wavelength of the X-ray radiation and β is the angle width at half-maximum height and θ is the half diffraction angle of the centroid of the peak in degree.

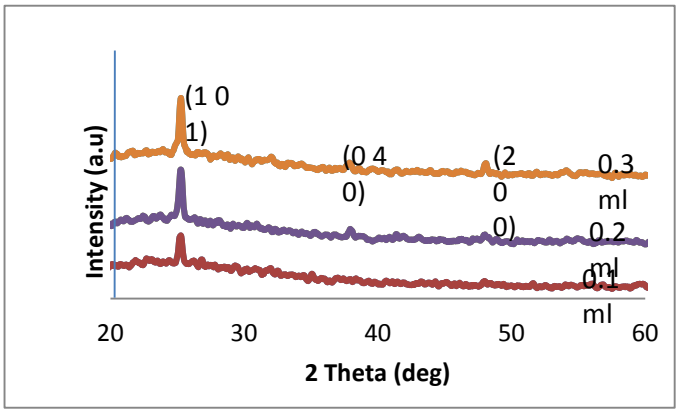


Fig. 1 XRD pattern of SiO_2:TiO_2 thin films for various concentrations

It is evident from Figure 1 that the dopant has a significant effect on the crystallite size of SiO_2:TiO_2 thin films. It also shows that the crystallite size of SiO_2:TiO_2 thin films prepared by the sol-gel technique and annealed at a temperature of 400°C decreases from 53.95nm to 33.17nm with increase in Si concentration [8]. Small proportion of SiO_2 is highly dispersed through the TiO_2 network homogeneously [5]. SiO_2 dopant effectively suppresses the phase transformation of TiO_2 from anatase to rutile [9].

The micro strain (ε) is calculated using the relation,

$$\varepsilon = \frac{\beta\,\mathrm{Cos}\theta}{4} \qquad (2)$$

The calculated values are tabulated in Table 1.It is observed that the micro strain exhibits an increasing tendency with SiO_2 dopant as it is dominated by β.

Consequently crystal dislocation is the main defect related to crystal size. The dislocation density is defined as the length of dislocation lines per unit volume of the crystal which was estimated from the following relation using Williamson and Smallman approach [10].

$$\delta = \frac{1}{D^2} \qquad (3)$$

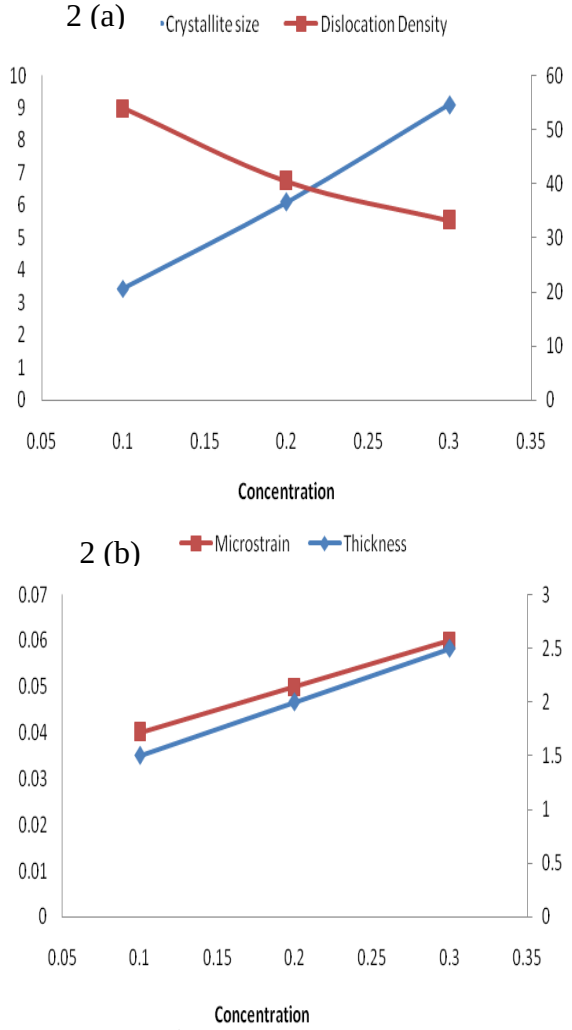


Fig. 2(a) Variation of crystallite size and Dislocation density & 2(b) Thickness and microstrain with different concentration of SiO_2

It was observed that the dislocation density increases with the increase in dopant concentration.

The number of crystallites 'N' was calculated using the relation

$$N = \frac{t}{D^3} \qquad (4)$$

where 't' is the thickness of the film. Figure 2(a) & (b) shows the variation of crystallite size, dislocation density, thickness and micro strain with concentrations.

TABLE 1: MICRO STRUCTURAL PARAMETERS OF TIO_2 THIN FILM FOR DIFFERENT DOPANT CONCENTRATION

Dopant concentration (ml)	Thickness (μm)	FWHM (β)	Crystallite size D(nm)	Dislocation Density δ x 10^{14} (lines/$m^{2)}$	Micro strain ε x10^{-3}	No of crystallites N x 10^{15}
0.1	1.5	0.1476	53.95	3.44	0.04	9.55
0.2	2	0.1968	40.47	6.1	0.05	30.2
0.3	2.5	0.2400	33.17	9.09	0.06	68.5

Optical Analysis

Figure 3 shows the transmittance spectra for different SiO_2 dopant concentration. The transmittance of doped thin film is in the visible range. At higher concentration of SiO_2 dopant, the scattering of photons increase due to the increased crystal defects and hence the transmittance decreases [11].

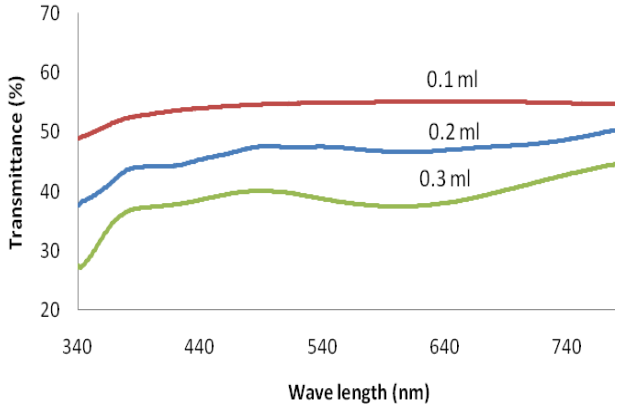


Fig. 3 Transmittance spectra of TiO_2 thin films for various concentration of SiO_2

The band gap energy [E_g] can be estimated from the optical absorption measurements. The plot of $(\alpha h\gamma)^2$ with photon energy ($h\gamma$) is shown in Figure 4(a). The optical absorption data recorded in Table 2 were analysed using equation (5) of optical absorption in semiconductor near band edge.

$$(\alpha h\gamma) = A\,(h\gamma - E_g)^{n} \qquad (5)$$

where A is a constant and E_g is the band gap value ; $h\gamma$ is the photon energy and n is a constant which depends on the probability of transition ; it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively. If the plot of $(\alpha h\gamma)^2$ Vs ($h\gamma$) is linear, the transition is direct allowed [Fig 4 (a)] and if $(\alpha h\gamma)^{1/2}$ Vs ($h\gamma$) is linear the transition is indirect allowed [Fig 4 (b)]. E_g can be determined by extrapolating the straight line portion at $\alpha = 0$. The band gap of the material is closely related to the wavelength absorbed; the wavelength of the light absorbed increases with decrease in the band gap [2].

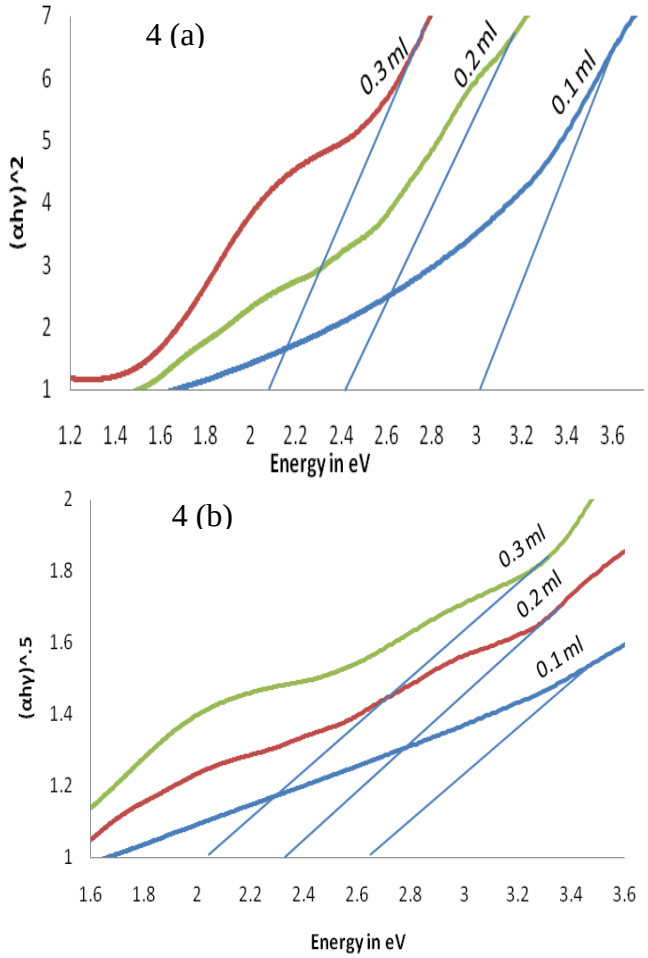


Fig. 4 (a) Direct (b) Indirect band gap of TiO_2 thin films for various concentration of SiO_2

The band gap of the material decreases from 3 eV to 2.1 eV with increase in SiO_2 concentration which indicates the improvement in the minimum energy required for excitation of electrons. The electrons can easily be excited from the valance band to conduction band [2]. The decrease in the band gap of the doped films is a promising factor for the potential application for TiO_2 - based material such as fabrication of Dye Sensitized Solar Cell (DSSC) [11]. The observed optical parameters are shown in Table 2.

The extinction coefficient of SiO_2:TiO_2 thin film was calculated from

$$K = (\alpha\lambda) / (4\,\Pi) \qquad (6)$$

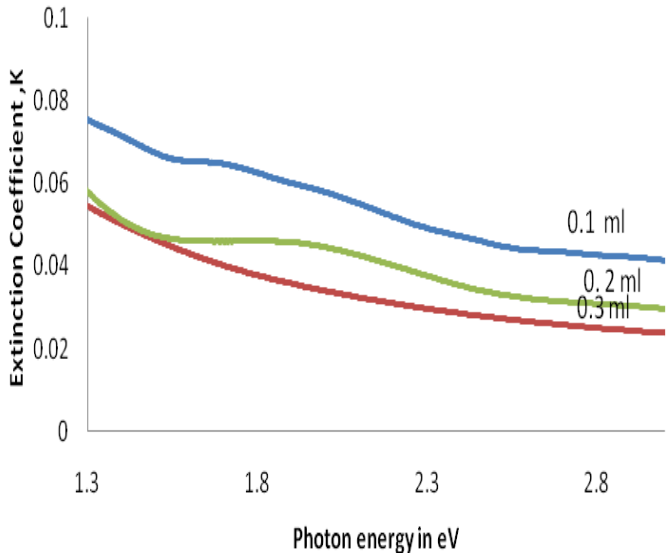


Fig. 5: Variation of extinction coefficient with concentrations

From Figure 5, it is observed that the extinction coefficient decreases as the photon energy increases [12]. It is noticeable that there is a decrease in the extinction coefficient with increasing concentrations of SiO_2.

TABLE 2: OPTICAL DATA OF SiO_2:TiO_2 THIN FILMS

Concentration of dopant (ml)	Direct band gap (eV)	Indirect band gap (eV)	Transmittance (%)	PL Intensity for peak at 485 nm	PL Intensity for peak at 560 nm
0.1	3	2.6	55	31	16
0.2	2.4	2.3	48	21	11
0.3	2.1	2	40	16	9

Photo Luminescence (PL)

The PL emission spectra is useful to disclose the efficiency of charge carrier trapping, immigration and transfer, and to understand the state of electrons and holes in semiconductor since PL emission results from the recombination of free carriers [13]. Figure 6 shows the PL spectra for SiO_2:TiO_2 thin film for various Si concentrations. The reduction of photo luminescence intensity with the increase in dopant concentration indicates the retardation of recombination process which is due to the efficient transfer of charge into highly dispersed nano sized SiO_2. Higher photo catalytic activity of doped film is obtained due to the lower recombination of electron and hole [11]. A decrease in the photo luminescence intensity indicates a lower recombination rate of electron hole pairs and higher separation efficiency [14]. Two main emission peaks appear at about 485 nm and 560 nm wavelength. The variation in PL intensity is the result of defect state on the shallow level of the TiO_2 surface [13].

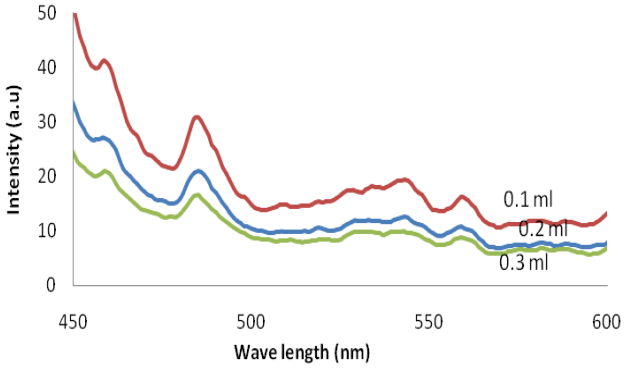
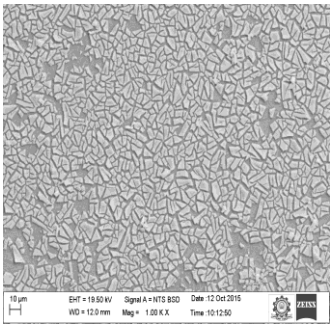


Fig. 6 PL spectra of the SiO_2:TiO_2 thin films for various concentrations

Morphological studies and EDAX analysis

The morphology of the thin film was analyzed by scanning electron microscopy. Figure 7 (a) & (b) show the SEM micrographs for 0.1ml and 0.3ml of SiO_2 dopant respectively. The results produced by this analysis 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 coefficients of expansion of the over layer and substrate [15]. The morphology of the films strongly depends on the concentration of dopant. At higher doping concentration, the growth of grain is suppressed and segregated due to the presence of compressive stress in the film [11].

7 (a) 7 (b)



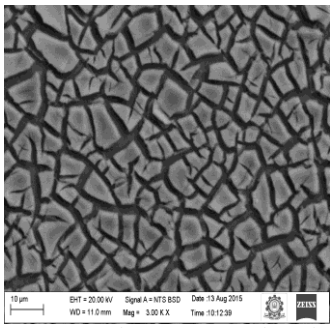


Fig. 7 SEM micrograph of SiO_2:TiO_2 thin films for (a) 0.1 ml and (b) 0.3 ml concentrations

Composition of the films was studied by EDAX analysis. In Figure 8 (a) & (b), the spectrum evidences the presence of SiO_2 along with Ti and O respectively for 0.1ml and 0.3ml Si concentration.

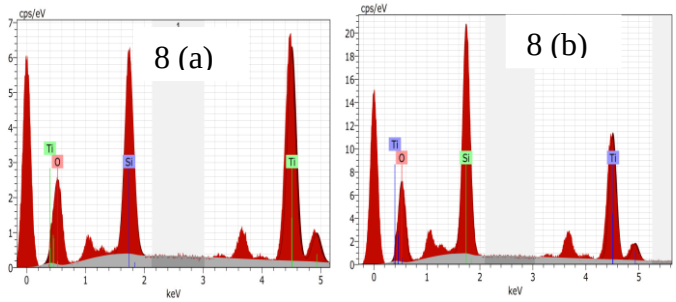
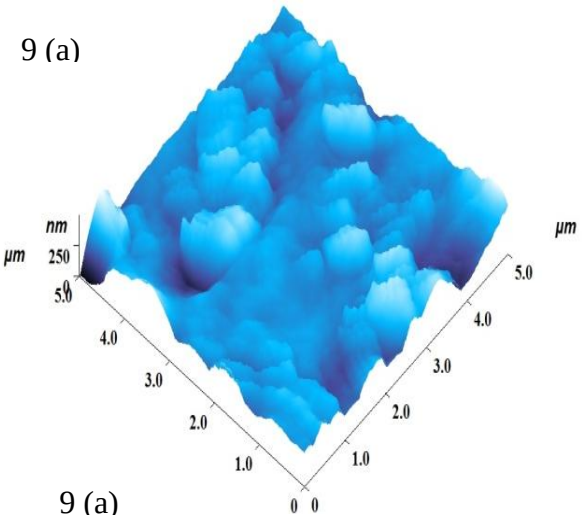


Fig. 8: EDAX Spectrum of SiO_2 :TiO_2 thin films for (a) 0.1 ml and (b) 0.3 ml concentrations

Surface Topography:

Atomic Force Microscopy (AFM) was used to characterize the surface roughness of the thin films. Figure 9 (a) and (b) show the AFM images (3D and 2D) of TiO_2 thin film doped with 0.2ml of Si. Scanning was carried out in semi contact mode with 0.5 µm X 0.5 µm areas.



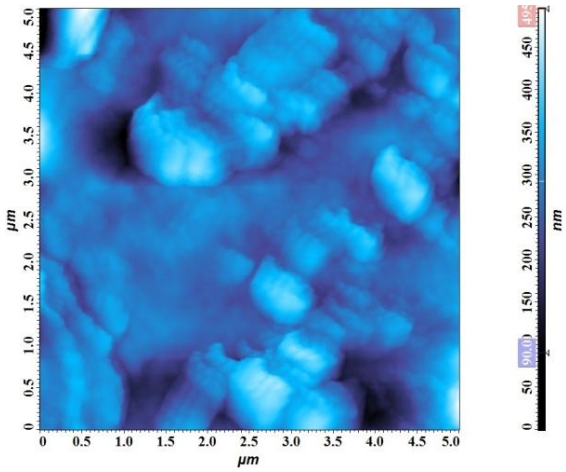


Fig. 9 AFM micrograph for SiO_2:TiO_2 thin film for 0. 2ml

Films are homogeneous in nature and well packed between the particles. 3D images show mountain and valley like structure. The root mean square and roughness values of the film were 41.2 nm and 31.9 nm respectively.

IV. Conclusion

This study focused on the effect of concentration of dopants on phase transformation, crystallite size, band gap and PL intensity of the SiO_2:TiO_2 thin film. XRD pattern of the SiO_2:TiO_2 film reveals the tetragonal structure with preferential orientation along (101) plane. The decrease in band gap was due to SiO_2 dopant. The PL intensity decreases with increase in dopant and it was attributed to the retardation of recombination process. Thickness of the film increases as the doping concentration increases. The stoichiometric ratio was confirmed with EDAX spectra. The results confirm that dopant has strong effect on structural and optical properties of nano crystalline thin films.

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