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EFFECT OF ANNEALING TEMPERATURE ON STRUCTURAL AND OPTICAL PROPERTIES OF CU-TIO_2 THIN FILM

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Abstract: Copper doped Titanium dioxide (Cu-TiO_2) thin films have been deposited onto the microscopic glass substrates by sol-gel dip coating method. The influence of annealing temperature was studied by X-ray diffraction method (XRD), Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Analysis (EDAX), UV-Vis absorption spectroscopy (UV-Vis-NIR), and Photoluminescence (PL) study. The XRD study revealed that Cu doped TiO_2 thin films have anatase phase with dominant (1 0 1) orientation. The crystallite size was found to increase with increase in annealing temperature. Morphological studies showed that the grains were agglomerated and island like structure over the entire surface of the substrate. The elementary compositions of the films were observed by EDAX spectrum. The UV-Visible spectral analysis showed that the calculated band gap values were found to decrease with increase in annealing temperature. Intense blue and green emissions were observed in photo luminescence spectrum at room temperature with excitation at 410 nm. These results suggest that the increase in annealing temperature is an important parameter for the improvement of structural quality of Cu - TiO_2 thin films derived by sol-gel dip coating technique.

Keywords: Cu-TiO_2 thin film, Sol-Gel, Dip Coating Technique, XRD, SEM, EDAX, UV-Visible and PL.

I. INTRODUCTION

Transparent conducting oxides (TCOs) are extensively used for a variety of applications including architectural windows, solar cells, flat-panel displays and polymer based electronics. This can be achieved by the development of transparent and conducting oxides (TCO) coatings such as tin oxide (SnO_2) [1], zinc oxide (ZnO) [2], Nickel oxide (NiO) [3] and titanium dioxide (TiO_2) [4]. Among these, TiO_2 plays a most promising role in several areas of recent research because of its high efficient photo catalytic activity, high refractive index, resistance to photo corrosion, chemical stability, low cost and non-toxicity [5]. One of the efficient ways of improving the properties of TiO_2 film is the addition of certain dopants. In recent years, many studies have been devoted to further improve the photocatalytic and antibacterial properties of TiO_2 thin films and the investigations suggest that those properties can be enhanced by doping with transition metal such as Ag [6], Fe^{3+} [7], N [8] and Cu [9]. TiO_2 films can be prepared by several methods such as sol-gel [10], chemical vapour deposition [11], spray pyrolysis [12], screen printing [13] and sputtering [14]. Among all, sol-gel is one of the most preferable techniques due to several advantages such as simplicity, homogeneity, low cost and easier coating on large areas.

In this work investigation into the effect of annealing temperature on structural, surface morphological and optical properties of Cu-TiO_2 thin films coated by sol-gel dip coating technique is reported.

II. EXPERIMENTAL PROCEDURE

The sol-gel dip coating method is basically a chemical deposition technique where the desired material is dipped onto the substrates by dip coating. Prior to deposition the substrates were cleaned with soap solution, acetone and then heated in chromic acid and kept in distilled water. Finally the substrates were ultrasonically cleaned for 30 minute. The dip coating method was used to prepare Cu-TiO_2 thin films on glass substrates using Titanium tetra isopropoxide (TTIP, 99.95% sigma - Aldrich), Copper II nitrate trihydrate (Cu $(NO_3)_2\,3H_2O$) as precursor solutions. The flowchart for the preparation Cu-Tio_2 thin films is shown in figure 1.

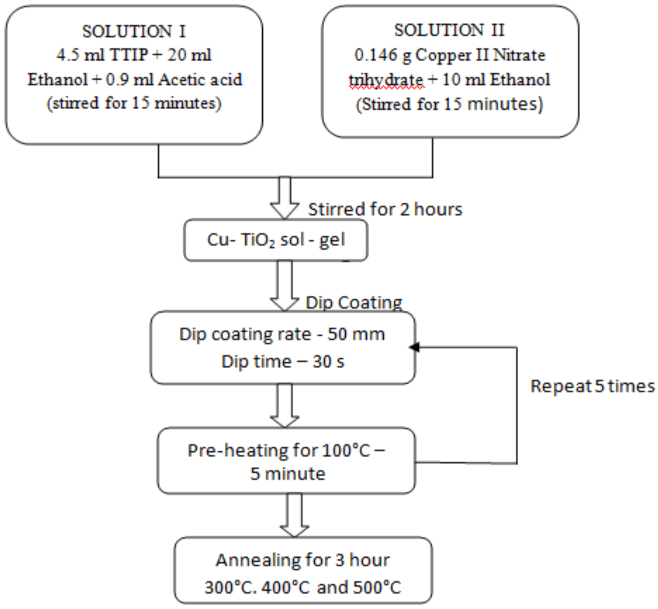


Figure1. Flow chart for the preparation of Cu-TiO_2 thin film

Annealing temperature is one of the parameters, which influence the properties of the thin films. The various annealing temperature (300°C, 400° C and 500°C) had been investigated by adding 0.5 mol% of Copper in TiO_2.

The crystallites of Cu doped TiO_2 thin films obtained for various annealing temperature were characterized by X-Ray diffraction (XRD) using X'PERT-PRO X - ray diffractometer which was operated at 40 KV and 30 mA with $CuK_{\alpha 1}$ radiation of wavelength 1.5406 A°. The surface morphological observations and elemental analysis were done by EV018 Carlzeiss SEM and S-Flash 6130 Bruker EDAX respectively. The thickness of the films was measured using Surfest SJ-301 (Stylus profilometer). UV-Visible spectra were recorded in the range of 400 - 700 nm by using the (Schimadzu 1800) UV-VIS-NIR spectrophotometer. The Photoluminescence (PL) spectra were recorded using (Schimadzu RF - 5301) luminescence spectrophotometer with xenon lamp as the light source at room temperature with an excitation wavelength of 410 nm.

III Results and Discussion

Structural Analysis

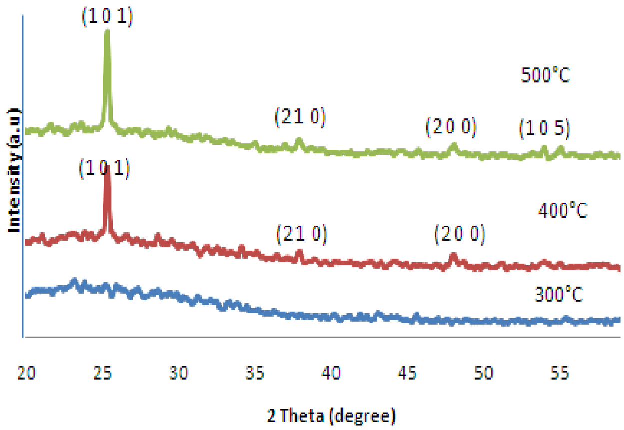


Figure 2: XRD Patterns of Cu-TiO_2 thin films with different annealing temperature

The XRD patterns of Cu doped TiO_2 thin films grown by dip coating method on glass substrates for different annealing temperatures 300°C, 400°C and 500°C was shown in figure 2. From the XRD pattern, it is observed that the Cu doped TiO_2 thin films have preferrential orientation along (1 0 1) plane which corresponds to tetragonal crystal structure of anatase phase. The observed XRD pattern is in good agreement with standard data JCPDS file no: 89-4203.

The crystallite size of the films were determined using Debye-Scherrer formula

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

where, D is the average crystallite size, λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of the dominant peak and θ is the Bragg angle. From the figure it is observed that the film was amorphous at annealing temperature 300°C. While increasing the annealing temperature, the intensity of the plane A (1 0 1), A (2 1 0) and A (2 0 0) increases along a plane A (1 0 5) due to increasing nucleation and growth of the films which exhibits the improved crystalline structure. Lin et.al. also showed that the film is amorphous in nature at lower temperature [15]. The inter-planar spacing (d_{hkl}) and the lattice constant (a & c) was calculated and the values were consistent with the standard values. The calculated unit cell parameters a = 3.787 Å and c = 9.484 Å are nearly equal to the standard value a = 3.784 Å and c = 9.514 Å (JCPDS no: 89-4203). Using the size of the crystallites, the dislocation density δ, strain ε and the number of crystallites per unit surface area N of Cu-TiO_2 thin films had been calculated.

The dislocation density (δ) was calculated using the relation

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

From the calculation it is observed that 'δ' decreases with increasing annealing temperature which implies decrease in lattice imperfection due to increase in crystallite size. The micro strain (ε) was calculated from the relation

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad (3)$$

The strain gets lower for increasing annealing temperature gives the best crystalline structure. The number of crystallites per unit surface area was calculated using the relation

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

The calculated crystallite size, dislocation density and strain for different annealing temperature are listed in Table.1. It shows that the crystallite size increases and the defects like dislocation density and strain in Cu-TiO_2 thin films decreases with increasing annealing temperature.

TABLE.1. MICROSTRUCTURAL PARAMETERS OF ANATASE (1 0 1) PLANE OF CU-TIO_2 FILMS DEPOSITED AT DIFFERENT ANNEALING TEMPERATURE

Annealing temperature	Thickness (μm)	Crystallite size D (nm)	Dislocation Density δ x 10^{14} (lines/m^2)	Micro Strain ε x 10^{-3}

400°C	1.13	54.26	3.396	36.29
500°C	2.32	58.14	2.958	34.66

3.2 surface morphology with Elemental analysis

The surface morphology of dip coated Cu doped TiO_2 thin films were investigated using Scanning Electron Microscopy technique. Figure 3a and 3b show the SEM image of Cu doped TiO_2 thin films at 400°C and 500°C respectively. From SEM image, it is observed that the Cu doped TiO_2 thin films at 400°C is loosely agglomerated and island like structure. Increase in temperature results in nucleation over growth and the film surface observed to be closely packed. It is understood that the shape and arrangement of the grains were influenced by the growth mechanism.

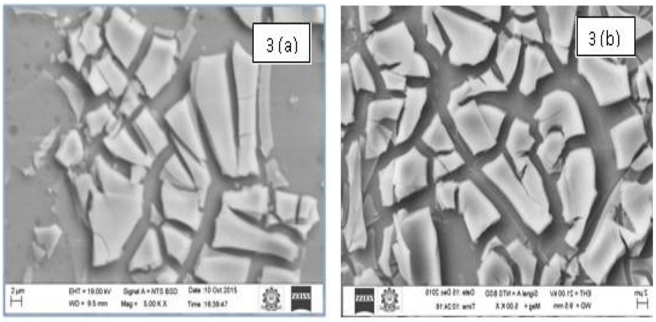


Figure: 3 SEM analysis of Cu-TiO_2 thin films for (a) 400°C (b) 500°C

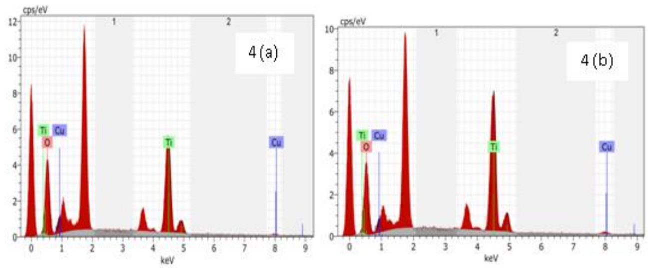


Figure 4: EDAX analysis of Cu-TiO_2 thin films for (a) 400°C (b) 500°C

The surface composition of the films was identified by EDAX measurement. The EDAX results are shown in figure 4a and 4b which demonstrates the presence of Ti, O and Cu in the spectrum.

Optical Analysis

The optical transmittance spectra of Cu doped TiO_2 thin films on glass substrate by dip coating technique was measured by UV-Vis spectrophotometer. Figure 5 shows the optical transmittance spectra of Cu doped TiO_2 thin films for 400°C and 500°C. The optical transmittance of the deposited film is about 50% for 400°C. As shown in figure, a gradual increase in transmittance was observed with an increase of wavelength from 400 nm to 650 nm. From the transmittance spectrum, it is also observed that the transmittance begin to fall off at a wavelength of about 390 nm and approaches to zero at 350 nm. The decrease in transmittance is due to the absorption of light that had caused the excited electron to immigrate from valence band to the conduction band of Cu-TiO_2 nanoparticles [16]. The optical transmittance decreases with increase in annealing temperature which is due to increase in film thickness and scattering of photons by crystal defects [17].

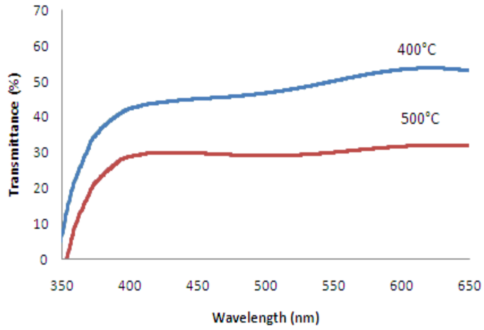
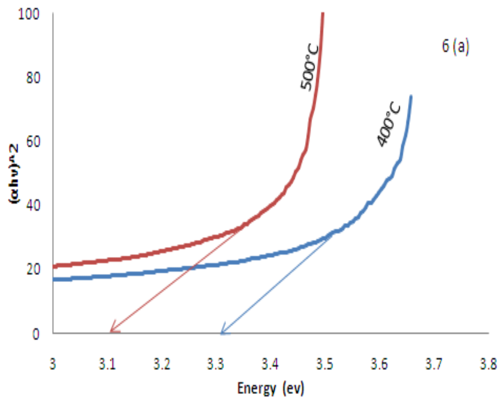


Figure 5: Transmittance spectra of Cu-TiO_2 thin films with different annealing temperature

The energy gap E_g (direct and indirect) of the Cu-TiO_2 thin films was calculated by plotting $(\alpha h\nu)^2$ versus $(h\nu)$ (figure 6a and 6b), then extrapolating the straight line part of the plot to the photon energy axis. The relationship between the absorption coefficients α and the incident photon energy hν is given by

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

Where E_g is the separation gap between bottom of conduction band and top of valence band, hν is the photon energy and n is the constant, which depends on the probability of transitions, it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden respectively.



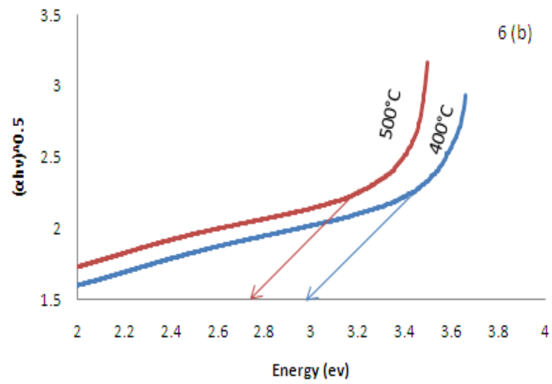


Figure: 6 (a) Direct and 6(b) Indirect band gap of Cu-TiO_2 thin films with different annealing temperature

The energy band gap (E_g) values for direct and indirect band gap for Cu-TiO_2 thin films were summarized in table 2. From the figure it is observed that the band gap (E_g) decreases with increase in annealing temperature and the values are listed in table 2. Annealing led to increased levels of localized near valence band and conduction band which is attributed to decrease in the energy gap of Cu-TiO_2 thin film [18].

The extinction coefficient of Cu doped TiO_2 thin films were calculated from

$$K = \frac{\alpha\lambda}{4\pi} \qquad (6)$$

where 'α' is the absorption coefficient and 't' is the thickness. Figure 7 shows the extinction coefficient of Cu doped TiO_2 thin films deposited on glass substrate for 400°C and 500°C. It is observed that the extinction coefficient increases with increase in temperature and it behaves the same as absorption.

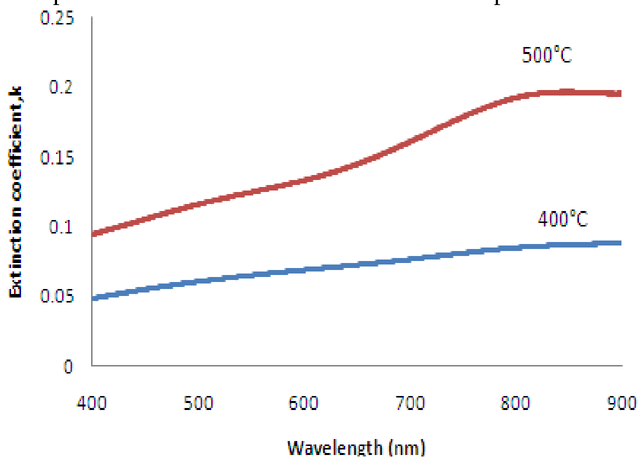


Figure: 7 Extinction coefficient Vs Wavelength for Cu-TiO_2 thin films with different annealing temperature.

The value of refractive index, n was calculated using the relation

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - K^2} \qquad (7)$$

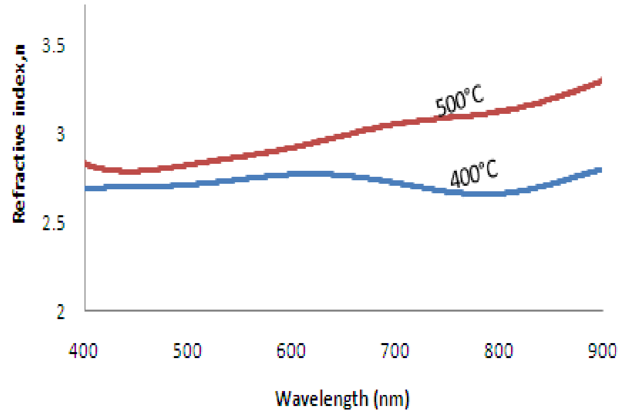


Figure: 8 Refractive index Vs Wavelength for Cu-TiO_2 thin films with different annealing temperature.

Figure 8 shows the variation of refractive index (n) of Cu-TiO_2 thin films in the wavelength range of 400-900 nm. The increase in the annealing temperature results in an increase in refractive index and is given in table 2. This increase is due to increase in film thickness and crystallite size [19].

The optical conductivity was calculated from the relation

$$\sigma = \frac{\alpha n c}{4\pi} \qquad (8)$$

The variation of optical conductivity with energy of Cu-TiO_2 with different annealing temperature is shown in figure 9. The optical conductivity increases with increase in temperature. This is due to the fact that at higher annealing temperature, the band gap between the valence band and conduction band became smaller and consequently, smaller photon energy was used by electrons to be excited from valence band to conduction band [16].

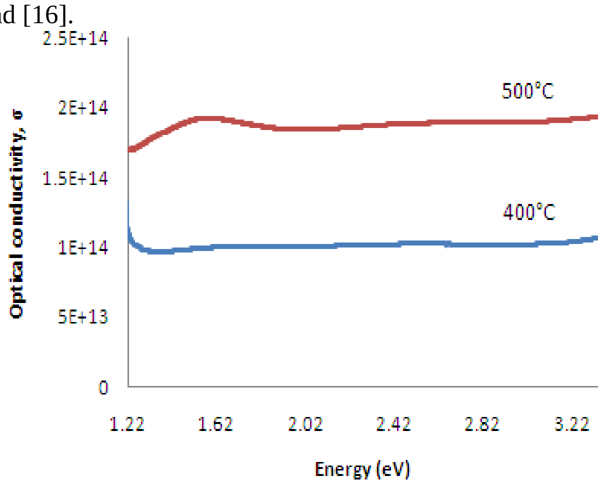


Figure: 9 Optical conductivity as a function of energy of Cu-TiO_2 thin films for different annealing temperature

TABLE 2: OPTICAL DATA OF CU-TiO_2 THIN FILM

Annealing Temperature	Optical Band gap (eV)		Refractive index, n	Optical conductivity, σ
	Direct	Indirect		
400°C	3.3	3.0	2.7	1.0

500°C	3.1	2.8	3	1.8

Photoluminescence:

Photoluminescence (PL) spectra of Cu-TiO_2 thin film had been recorded at room temperature with an excitation wavelength of 410 nm. Figure 10 shows the PL spectra of Cu doped TiO_2 thin films at different annealing temperature. The blue band emission at 485 nm (2.6 eV) is attributed to excitonic transitions. The green band peak at 560 nm (2.2 eV) corresponds to TiO_2 anatase phase. The intensity of photoluminescence decreases with increasing temperature. This indicates a lower recombination rate of electron-hole pairs and hence higher separation efficiency [20].

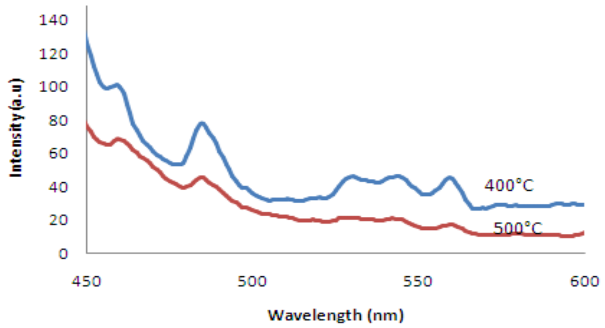


Figure: 10 Photoluminescence spectra of Cu-TiO_2 thin films with different annealing temperature

IV. Conclusion

Cu doped TiO_2 thin films had been deposited successfully onto glass substrate using sol-gel technique for various annealing temperature. X-ray diffraction analysis revealed that the prepared films were tetragonal structure of anatase phase with preferential orientation along (1 0 1) plane. Also the micro structural parameters such as crystallite size, strain and dislocation density were estimated. The SEM pictures show island and small canals with mosaic like structure. EDAX analysis revealed that the films contain Ti, O and Cu elements. The transmittance of Cu-TiO_2 thin films annealed at 500°C has the least transmittance due to film thickness. The increasing annealing temperature causes a decrease in the optical band gap value and an increase in the optical constants such as refractive index (n), extinction coefficient (K) and optical conductivity (σ). These results suggest that the increase in annealing temperature is an important parameter for the improvement of structural and optical quality of Cu-TiO_2 thin films derived by sol-gel dip coating technique.

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