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Optical Properties of Al-Doped TiO_2 Thin Films

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Abstract

Un-doped titanium dioxide (TiO_2) and aluminium (Al) doped thin films were prepared by the sol-gel method. TiO_2 sol is mixed with different weight % of aluminium and films were prepared by spin coating. The films were characterised with optical transmittance/reflectance measurements using spectrophotometer. The optical constants (n, k) were determined by envelope method. Optical band gap energy was estimated using Tauc's method and found to be 3.36 and 3.28 eV respectively at 50°C and 150°C respectively.

Keywords:

TiO_2;
Sol-Gel;
Optical properties;
n & k;
Thin films.

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1. Introduction

The sol-gel method is an important cost effective chemical method of preparation of metal oxides [1-3], dielectric and perovskite nanomaterials [4-6]. TiO_2 thin film is used in various applications because of its unique physical and chemical properties such as high dielectric constant, large energy gap and high refractive index etc. TiO_2 thin film is an excellent nano material finds potential applications in various fields such as gas sensors, photo catalyst, CMOS devices, opto-electronic devices and antireflection coatings [7-9] etc. He et al [10] reported the preparation of nitrogen doped TiO_2 thin films by rf sputtering method. They studied the variation of optical constants and optical band gap energy with doping concentration and reported the increase in n and k values and decrease in optical band gap energy with increase of nitrogen doping content. Mohanty et al [11], studied the influence of tin doping on the optical and structural properties of TiO_2 thin films and reported the complete transformation from anatase to rutile phase after annealing at 500°C by the doping of Sn. Kim et al [12] reported the effect of Al doping on the growth behaviour of TiO_2 thin films prepared by atomic layer deposition. Vishwas et al.[13] reported the preparation of anatase TiO_2 thin films by the sol-gel method after annealing at 300^{o}C and higher. In this article, the preparation of un-doped and Al doped TiO_2 thin films by the sol-gel method and some studies on optical properties of these thin films have been presented.

2. Experimental procedure

TiO_2 and Al-doped TiO_2 thin films were synthesised by the sol-gel spin coating using titanium (IV)isopropoxide and aluminium chloride ($AlCl_3$) as the precursor materials of TiO_2 and Al, respectively and absolute ethanol used as a solvent. The precursor of TiO_2 and solvent were mixed in the volume ratio of 1:9 and stirred constantly for 3 hours using a magnetic stirrer. A few drops of concentrated HCl was used as a catalyst [14], which follows the reaction [15],

$Ti\,(OR)_4 + H_2O \rightarrow Ti(OR)_3\,(OH) + ROH$

$Ti(OR)_4 + Ti(OR)_3\,(OH) \rightarrow Ti_2\,O(OR)_6 + ROH$

The reaction stops with inclusion of two water molecules

$Ti\,(OR)_4 + 2\,H_2O \rightarrow TiO_2 + 4ROH$

$Ti(OC_3H_7)4 + 2H_2O \rightarrow TiO_2 + 4C_3H_7OH$

The sol was kept in an air tight beaker for one hour for hydrolysis and polycondensation of titanium alkoxide. The resultant gel was spin coated on pre-cleaned glass and p-silicon (001) substrates. A part of gel was mixed with different wt. % of Al using $AlCl_3$ and Al doped TiO_2 films were prepared on p-silicon substrates. The flow chart for the preparation of TiO_2 thin film is shown in Fig.1. Un-doped TiO_2 films were annealed at different temperatures and subjected to optical characterization with optical transmittance/reflectance measurements using UV-VIS-NIR spectrophotometer (Ocean optics, USA) in the wavelength range 300 - 1000 nm.

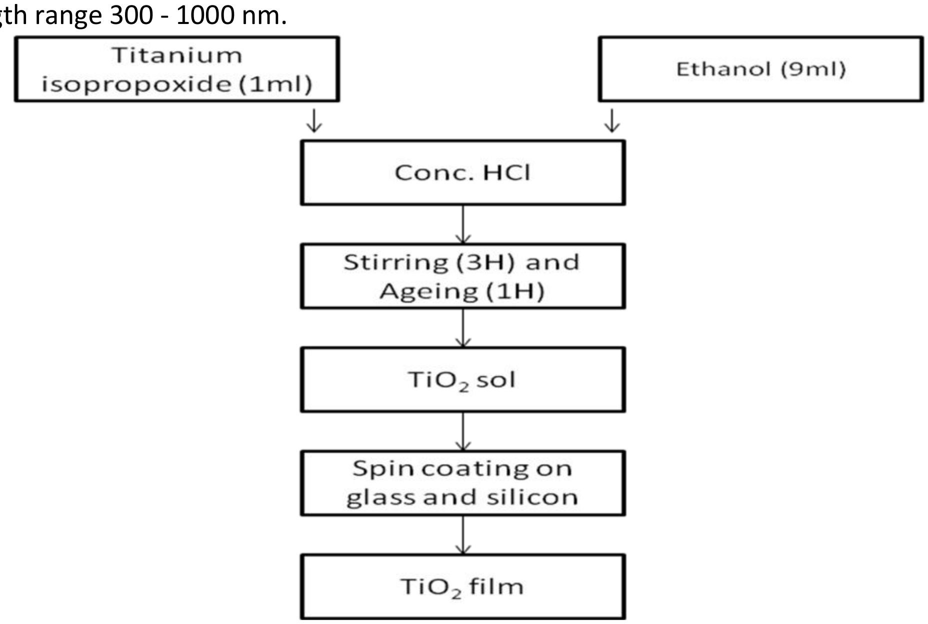

Fig.1. Flow chart for the preparation of TiO_2 thin films by the sol-gel method.

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3. Results and discussions

Optical transmittance spectra of TiO_2 films deposited on glass substrates annealed at different temperatures is as shown in Fig. 2. The transmittance decreased with increasing the annealing temperature. This is due to the densification of the films [16]. The optical absorption in the film increases with increase of density of the film. The film thickness was estimated to be 148 nm, 137 nm and 133 nm, respectively after annealing the film at 50, 150 and 200^{o}C. The refractive index of TiO_2 film was found to be 2.02, 2.05 and 2.07 (measured at 550 nm) and extinction coefficient as 0.003, 0.005 and 0.009 for the films annealed at 50, 150 and 200^{o}C, respectively estimated by envelope method [17].The refractive index and extinction coefficient of TiO_2 film increased with increase of annealing temperature.

The optical band gap energy of TiO_2 film estimated by Tauc plot is as shown in the Fig.3. It is observed from the figure that the optical band gap energy of TiO_2 film annealed at 50^{o}C and 150^{o}C is 3.36 and 3.28 eV, respectively. Hence, the optical band gap energy decreased with increase of annealing temperature.

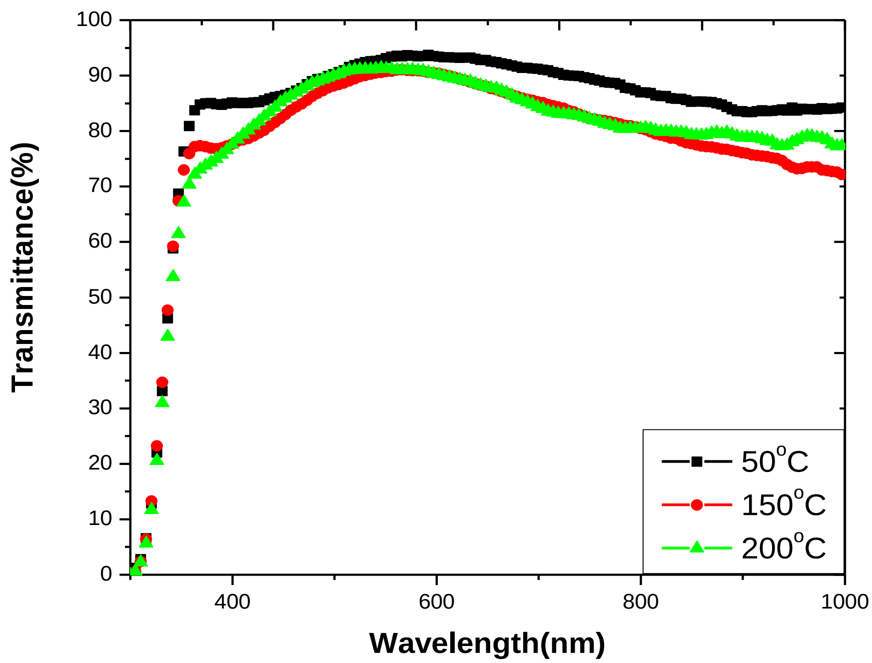

Fig. 2. Optical transmittance spectra of TiO_2 films annealed at different temperatures in air.

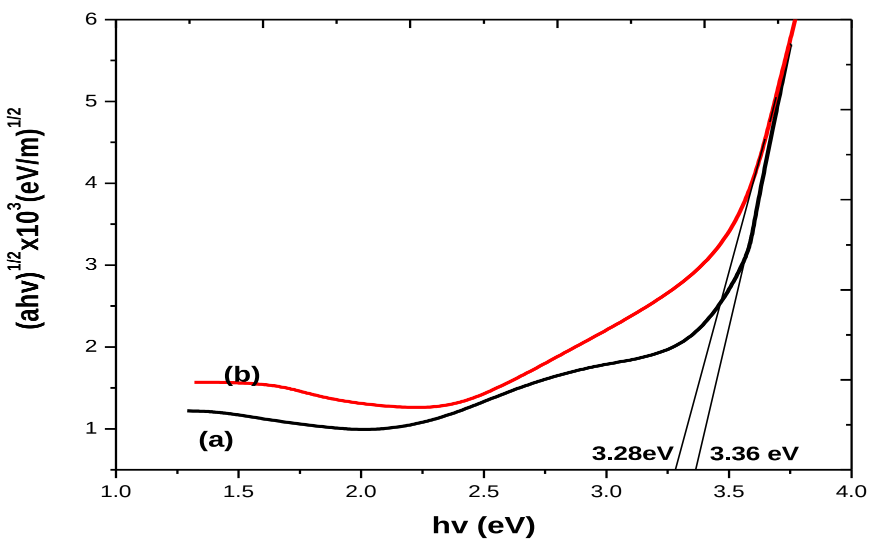

Fig. 3. Tauc plot for TiO_2 film annealed at (a) 50^oC and (b) 150^oC in air.

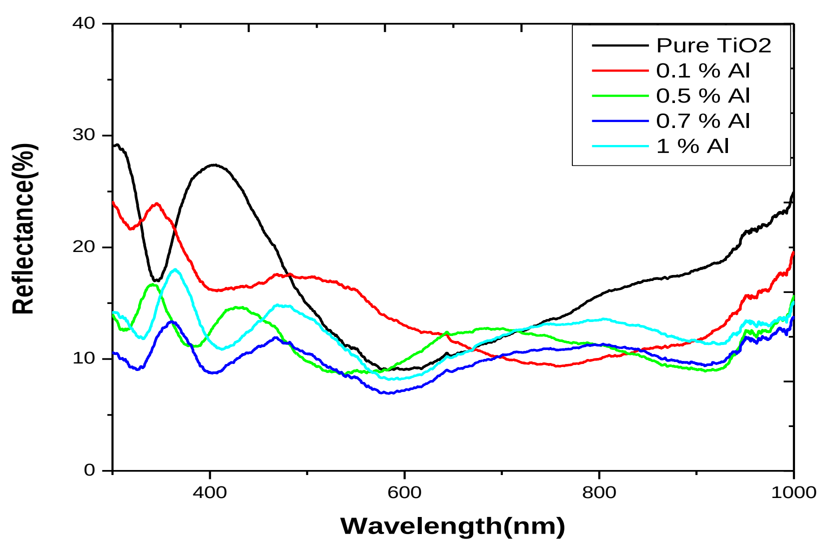

Fig. 4. Optical reflectance spectra of un-doped and Al doped TiO_2 films.

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The reflectance spectra of the un-doped TiO_2 film and the films doped with different wt. % of Al prepared on p-silicon substrate is shown in Fig. 4. The reflectance decreased with increasing the concentration of Al in TiO_2 sol. The film thickness increased with increase of Al concentration. The increase of film thickness may be due to the increase of porosity in the film. The decrease of reflectance is also due to the increase of porosity in the film [18].

Equations

The thickness of the films has been calculated using the relation

$$t = \lambda_1 \lambda_2 / 2n (\lambda_2-\lambda_1) \quad (1)$$

where λ_1 & λ_2 are wavelengths corresponding to successive maxima/minima in reflectance spectra.
The refractive index was calculated using the relation

$$n = (n_o n_s) [1+ (R_\lambda)^{1/2} / 1- (R_\lambda)^{1/2}]^{1/2} \quad (2)$$

where n_o & n_s are refractive indices of air & substrate, R_λ is the reflectance maxima.
The absorption coefficient "α" is calculated using the relation

$$\alpha = (1/ t) \ln (1/ T) \quad (3)$$

where t and T are the film thickness and transmittance (%), respectively. The extinction coefficient is measured using the relation

$$K = \alpha \lambda / 4\pi \quad (4)$$

The thickness and refractive index of the films were calculated using the equations (1) and (2) and presented in table 1. The refractive index of the TiO_2 films decreased with increasing the wt % of Al.

Table 1- The refractive index and thickness of TiO_2 and Al doped TiO_2 films

Film	λ_{max-1} (nm)	R_{max-1}	n	Thickness t (nm)
TiO_2	406.0	0.273	2.186	167.9
0.1% Al	345.4	0.238	2.087	273.6
0.5% Al	341.0	0.166	1.887	449.2
0.7% Al	361.8	0.133	1.795	442.6
1% Al	363.1	0.179	1.923	409.8

4. Conclusions

Un-doped and Al doped TiO_2 thin films were prepared by the sol-gel spin coating method. Effect of annealing temperature and Al doping on the optical properties of the TiO_2 films are studied. The decrease of optical transmittance with annealing temperature is due to the densification of the films. The reflectance spectra shows the decrease of reflectance with increase of Al concentration up to 0.7 wt. % and reflectance increased for 1 wt.% of Al. The refractive index of the films decreased with increasing Al concentration. The refractive index and extinction coefficient were decreased with wavelength. The refractive index and extinction coefficient increased with increasing the annealing temperature due to increase of density of the film. Indirect band gap energy was found to be 3.36 eV & 3.28 eV at the annealing temperature of 50^oC and 150^oC, respectively. Hence the band gap energy was decreased with annealing temperature which signifies the semi conducting nature of TiO_2 film.

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