

Characteristic comparison of TiO₂ thin films with an inorganic and organic precursor at different molarities by Spray pyrolysis

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ABSTRACT : TiO₂ thin films were deposited by spray pyrolysis technique using TiCl₃ and TiAcAc as precursors on glass substrate. The structural and optical characteristics have been studied with variation of precursor concentration and precursor. XRD showed the structural orientation of the films especially in (101) plane corresponding anatase phase of TiO₂. Band gap energy, refractive index, extinction coefficient and dielectric constants were estimated from U-V absorption data. The variations of these optical parameters with molar concentrations and precursors had been studied. The intense green light emissions for the films at 0.05M and 0.1M for InCl₃ precursor and U-V and violet emission for the films at 0.05M and 0.1M for TiAcAc precursor were observed in the PL spectra.

KEYWORDS: TiAcAc, Pneumatic, Dielectric constant, organometallic.

I. INTRODUCTION

Titanium dioxide (TiO₂) or titania thin films are widely studied because of their fascinating chemical, electrical and optical properties [1,2]. TiO₂ film in anatase phase could achieve the photocatalytic degradation of organic compounds under the radiation of UV. So, it has a diversity of application views in the field of environmental protection [3,5]. TiO₂ thin film in rutile phase is known as a good blood compatibility material and can be used as artificial heart valves [5]. In addition, TiO₂ films are important optical films due to their high reflective index and transparency over a wide spectral range [2]. During the two last decades, several methods have been used for the TiO₂ thin films preparation, [6], sol-gel method [7], chemical vapour deposition [8], successive ionic layer adsorption and reaction (SILAR) [9], solvothermal [10], chemical bath deposition [11] and spray pyrolysis [12]. Among these methods, spray pyrolysis technique has got many advantages such as the low cost of the apparatus and source materials, accurate control over the deposition parameters and producing large area films deposition compared to other deposition methods.

TiO₂ films were deposited so far with Titanium (III) chloride (TiCl₃), Titanium (IV) Chloride (TiCl₄), Titanium (IV) isopropoxide Ti(OCH(CH₃)₂)₄, Titanium di-isopropoxydi-ethyl hexanoate(Ti(OC₃H₇)₂(C₇H₁₅COO)₂), Titanyl acetylacetonate (TiC₁₀H₁₄O₅) etc used as precursors. Among these precursors, Titanyl acetylacetonate (TiAcAc) is a predominant and TiCl₃ is an infrequent source material for TiO₂ films deposition.

In the present work we have compared the structural and optical characteristics of sprayed TiO₂ films with an inorganic precursor TiCl₃ and an organic or organometallic precursor TiAcAc at different molar concentrations. Initially the XRD characterization of deposited films at different temperatures at a constant precursor concentration is studied and the optimum temperature was fixed for both the precursors. Then the optimum molarity was found by various studies of deposited TiO₂ films for various precursor concentrations with this optimum temperature. The scope of this work is to optimize the molar concentration and precursor of highly transparent conductive TiO₂ films by comparing the characteristics.

II. EXPERIMENTAL DETAILS

TiO₂ films were deposited at different molarities for both the precursors by a pneumatic controlled spray pyrolysis. TiCl₃ and deionized water mixtures, TiAcAc and methanol mixtures were sprayed on to glass substrates with dimension of 75 x 25 mm². During our experiments we had varied the precursor concentration to 0.05M and 0.1M by keeping substrate temperature and other deposition parameters as constant. In the spray pyrolysis unit the substrate temperature was maintained with help of a heater and an electronic circuitry, which contains a thermal sensor with relay switch. The precursor solution and carrier gas assembly connected to spray gun was moved in the horizontal plane by means of pneumatic controlled system. The substrate to nozzle distance was maintained at 25cm with 45° angle. The films deposited on pre-cleaned glass plates were gradually cooled to room temperature and then rinsed with deionized water and dried. The obtained TiO₂ films were annealed at 500°C for 5 hours in stagnant air.

The well-adherent TiO₂ films underwent structural, optical studies. The structural studies were carried out by using on **Pan Analytic X'Part PRO** Powder X-ray diffractometer (XRD) equipped with Cu-K α radiation ($\lambda=1.5418\text{\AA}$). The optical absorption and photoluminescence spectra were recorded using **UV-VIS-Perkin Elmer's LAMBDA35** spectrophotometer and **Varian Carry ellipse** photoluminescence spectrometer respectively.

III. RESULTS AND DISCUSSION

3.1. Structural studies:

The XRD spectra of TiO₂ films for the molarities 0.05M and 0.1M for the precursor (i) TiCl₃ and (ii) TiAcAc are as shown in Fig.1. The XRD spectra of TiO₂ films deposited at various molar concentrations of 0.05M and 0.1M and heat-treated at 500°C for 5 hours are shown in Fig.1. The plots show polycrystalline nature with a noticeable (1 0 1) peak of TiO₂ at $2\theta = 25.28^\circ$. This peak corresponds to the tetragonal crystal structure of anatase phase with space group I41/amd. The observed 'd' value is in good agreement with the JCPDS Card No-21-1272. [13]. The lattice constants a and c have been determined from inter planar spacing of different (h k l) planes. The inter-planar distance between the lattice planes are consistent with the standard values and the calculated unit cell parameters $a=3.778\text{\AA}$, $c=9.681\text{\AA}$ are nearly equal to the standard values $a=3.785\text{\AA}$ and $c=9.513\text{\AA}$.

In the spectra, for the precursor TiCl₃ the film deposited at 0.05M, only the plane Anatase(101) is present. While increasing molarity to 0.1M, the intensity of A(101) plane is increased along with some new planes A(004) and A(200) are appeared due to increasing nucleation and growth of the films. For the precursor TiAcAc the film deposited at 0.05M, along with intense A(101) plane a new plane A(211) is appeared with less intensity. Further increasing of molarity to 0.1M, the intensity of A(101) plane is decreased. Among these films, TiCl₃ precursor 0.1M has A(101) plane with a very high intensity exhibiting the improved crystalline structure.

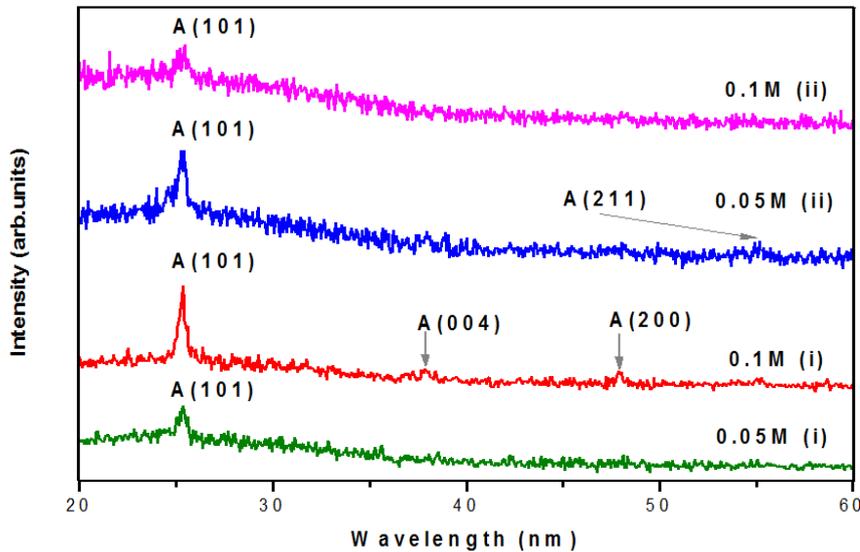


Fig.1.XRD Spectra of TiO₂ films at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc

The grain size calculations are carried out from the Scherer-Bragg equation

$$D = \frac{kl}{\beta \cos\theta} \quad (1)$$

The micro strain (ϵ) is determined with the relation:

$$\epsilon = \frac{\beta \cos\theta}{4} \quad (2)$$

The dislocation density (δ) is calculated using the relation:

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

The inter planar spacing (d_{hkl}) is calculated using the relation

$$d_{hkl} = \frac{n\lambda}{2 \sin\theta} \quad (4)$$

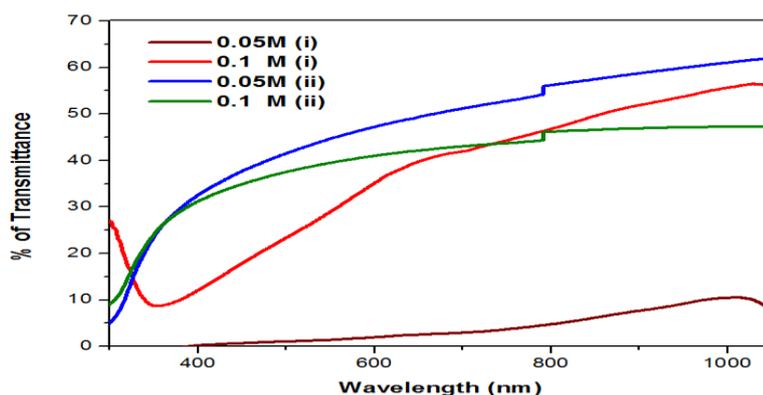
The parameters of (101) plane, for different molarities is listed in Table.1. It shows that the 0.1M with TiCl₃ precursor has favorable structural parameters rather than other films.

Table.1. microstructural parameters of anatase (101) plane of TiO₂films deposited at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc

Molar concentration	Grain size, D (nm)	Micro strain, ϵ x10 ⁻³	Dislocation density, δ x10 ¹⁵ (m ⁻²)	Inter- planar spacing (nm)
0.05M(i)	16.6	2.17	3.60	0.92
0.1 M (i)	20.7	1.74	2.31	1.12
0.05M(ii)	6.9	5.19	2.05	1.87
0.1 M (ii)	4.8	7.48	4.27	2.04

3.2. Optical properties of TiO₂films

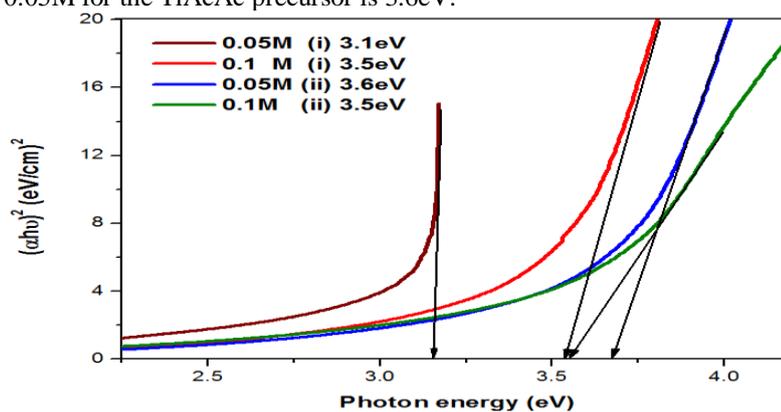
The optical transmittance spectra of TiO₂ films at the molarities 0.05M and 0.1M for the precursors (i) TiCl₃ and (ii) TiAcAc are as shown in fig.2 for the wavelength range of 300 nm to 1000 nm. The percentage of transmittance for all the films is minimum in UV region and maximum in the visible and near infra-red regions. The increasing transmittance percentage is due to uniform oxidation and improved lattice arrangements [14]. From the transmittance spectra, the transmittance percentage of the film at 0.1M for the TiCl₃ precursor is maximum than the film at 0.05M. For the TiAcAc precursor the transmittance percentage of the film deposited at 0.05M is maximum than the film at 0.1M. On comparing the precursors the transmittance percentage is maximum at 0.05M with TiAcAc precursor.


 Fig.2. Optical Transmission spectra of TiO₂ films at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc

The optical band gap of deposited TiO₂ films is evaluated from the relation between absorption coefficient α and photon energy $h\nu$.

$$(\alpha h\nu) = A (h\nu - E_g)^x \quad (6)$$

Where A is a constant, E_g is the optical band gap and $x=1/2$ for directly allowed electronic transitions. The fig.3 shows the plot between $(\alpha h\nu)^2$ and $h\nu$ of the deposited films at 0.05M and 0.1M for the precursors (i) TiCl₃ and (ii) TiAcAc. The extrapolation of linear portion of the curves on $h\nu$ axis gives the direct band gap energy. The spectra shows that the band gap energy of the films ranging from 3.1 eV to 3.6 eV. The increasing of band gap energy is accredited to the carrier density due to Brustein-Moss effect [15]. The high value of band gap energy for the film at 0.05M for the TiAcAc precursor is 3.6eV.


 Fig.3 Optical band gap spectra of TiO₂ films at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc

The extinction coefficient (k) can be determined using the relation

$$k = \frac{\alpha \lambda}{4\pi} \quad (7)$$

Fig.4 shows the variation of extinction coefficient with wavelength of TiO₂ films at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc. In this spectra, the films with the TiCl₃ precursor at 0.05M and 0.1M having maximum k in the U-V region, almost constant and minimum in the visible and near infrared regions. The films with the TiAcAc precursor at 0.05M and 0.1M having minimum k in the U-V region, almost constant and maximum in the visible and near infrared regions. Especially, the spectrum of the film at 0.05M for the TiAcAc precursor is revealed that the minimum value of k than the other films. The minimum of extinction coefficient or the index of absorption established that the films are highly transparent and without any crystallographic defects.

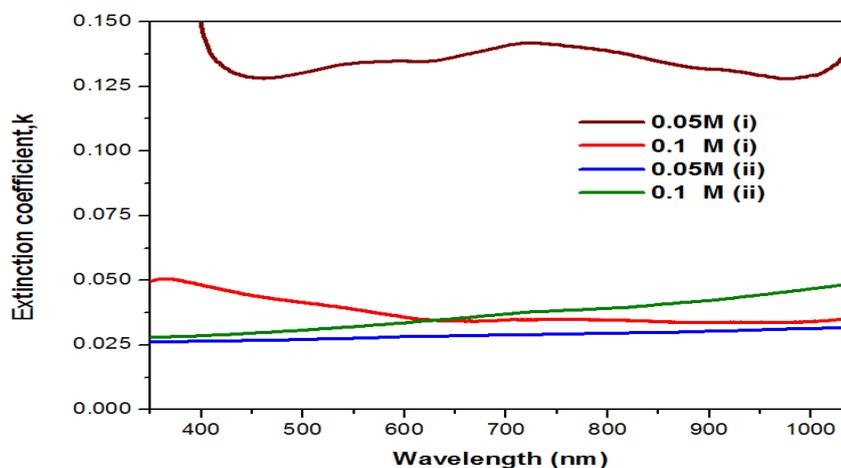


Fig.4. Variation of extinction coefficient with wavelength of TiO₂ films at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc

The refractive index (n) of the film can be evaluated using the relation

$$n = \frac{(1+R)^{1/2}}{(1-R)^{1/2}} \quad (8)$$

Where R is the normal reflectance. Fig.5 shows the variation of refractive index with wavelength of the films at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc. In these spectra for TiCl₃ precursor, the films deposited for 0.1M is having maximum refractive index 2.64 for the wavelength 680nm. The 0.05M exhibits different property as the maximum refractive index 2.64 in the U-V (199nm) and near infrared regions (1028nm) (not shown in Fig. 5). This may be due to the porosity and pinholes in the film surface with randomly oriented grains. For TiAcAc precursor the films deposited at 0.05M and 0.1M having maximum refractive index 2.65 and 2.64 for the wavelengths 533nm and 660nm respectively. On comparing all the films the refractive index is maximum at 0.05M for TiAcAc precursor and all the films exhibit their refractive index as minimum in the U-V region and maximum in the visible and near infrared regions.

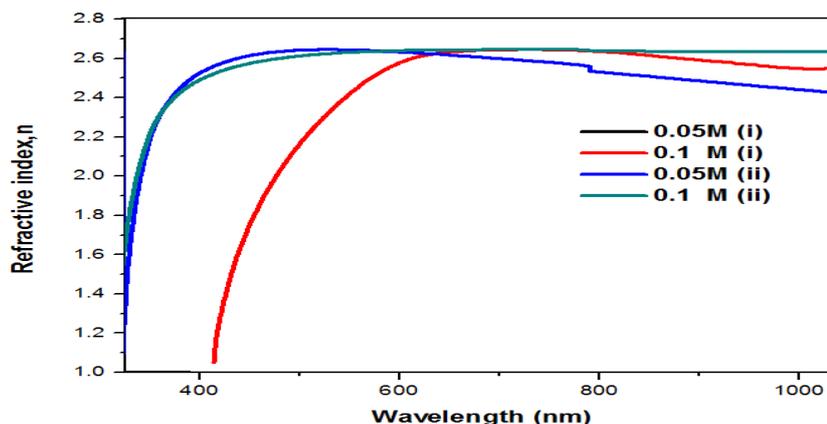


Fig.5. Variation of refractive index with wavelength of TiO₂ films at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc

The dielectric constant, ϵ of the films is determined by the relation

$$\epsilon = \epsilon_1 + \epsilon_2 = (\epsilon_1^2 + \epsilon_2^2)^{1/2} \quad (9)$$

$$\epsilon_1 = n^2 - k^2 \quad \text{and} \quad \epsilon_2 = 2nk \quad (10)$$

where, ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric constant.

The dielectric constant or the absolute complex permittivity of a material depends on temperature, pressure and frequency, etc. The frequency dependence of real and imaginary parts of the dielectric constant for the films at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAcis as shown in fig.6. From the figure, the films deposited for TiCl₃ precursor at 0.1M is observed to have the maximum value of real and minimum value of imaginary parts of the dielectric constant and for the molarity 0.05M the values of real and imaginary parts of the dielectric constant is not observed in the visible and near infra-red regions. For TiAcAc precursor the films deposited at 0.05M is observed to have the maximum value of real and minimum value of imaginary parts of the dielectric constant than the film at 0.1M. Above all the film at 0.05M for TiAcAc is observed to have the higher values of real and lesser values of imaginary parts of the dielectric constant than all the films, and it may be due electronic polarization of the material.

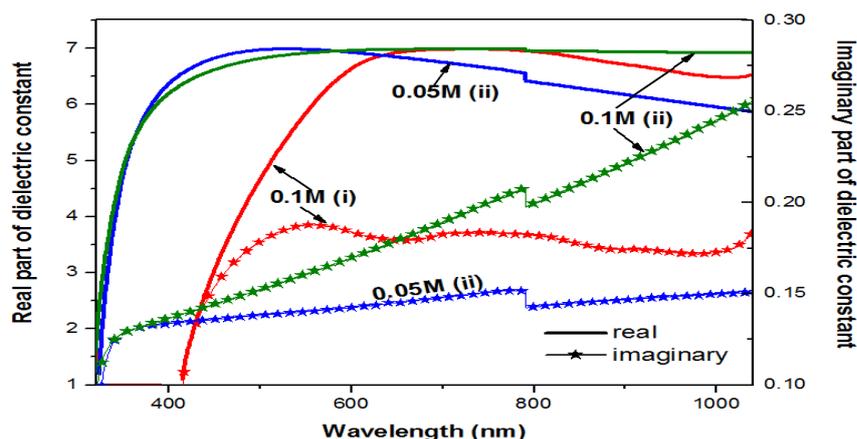


Fig.6. Variation of real and imaginary parts of the dielectric constant with wavelength of TiO₂ films at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc

The photoluminescence spectra of TiO₂ films were obtained using bombardment of an excitation source with wavelength of 325nm. The fig.7 shows the PL spectra of the films deposited at 0.05M and 0.1M for the precursors (i) TiCl₃ is in the wavelength range from 500nm to 550nm and (ii) TiAcAc is in the wavelength range from 300nm to 600nm. In the spectra, the films at 0.05M and 0.1M for the TiCl₃ precursor are exhibiting same emission spectra. They have one emission peaks corresponding green light at 520nm. But for the TiAcAc precursor the films at 0.05M and 0.1M, both are having only one emission peaks of U-V (396nm) and violet (409nm) regions respectively. From photoluminescence spectra of various molarities precursors, the intensity of PL emission is observed to be maximum for the film at 0.05M with TiAcAc precursor, which implies that more radiative recombination occurs with the excitation source of wavelength of 325nm. The observed optical parameters of TiO₂ films deposited at different molarities and different precursors are listed in Table.2.

Table.2. Optical parameters of TiO₂ films deposited at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc

Temperature	Band Gap energy(eV)	Refractive index	Extinction coefficient (minimum value)	Dielectric constant, real part	Dielectric constant, imaginary part	PL intensity (arb.units)
0.05M (i)	3.15	2.64	0.127	----	----	62.4
0.1 M (i)	3.54	2.64	0.033	7.00	0.187	62.5
0.05M (ii)	3.61	2.65	0.025	7.01	0.157	117.7
0.1M (ii)	3.48	2.64	0.027	6.99	0.478	73.1

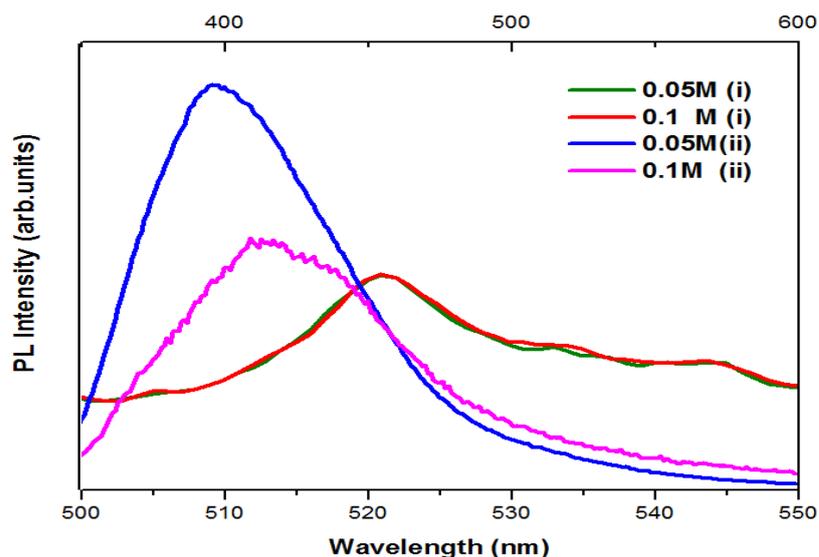


Fig.7. PL spectra of the TiO₂ films at different molarities for the precursors (i) TiCl₃ and (ii) TiAcAc

IV. CONCLUSIONS

The Titanium oxide (TiO₂) films were deposited by spray pyrolysis technique using an inorganic compound Titanium chloride (TiCl₃) and an organic compound Titanylacetylacetonate (TiAcAc) as precursors. The films were deposited at 0.05M and 0.1M for both the precursors and annealed at 500°C for 5 hours in stagnant air. On comparing the microstructural characteristics of the films at 0.05M and 0.1M for the TiCl₃ precursor, the film deposited at 0.1M has (101) plane with very high intensity exhibited that the improved crystalline structure, maximum of grain size and minimum of micro strain and dislocation density. On comparing the films at 0.05M and 0.1M for the TiAcAc precursor, the film deposited at 0.05M has favorable microstructural characteristics. In addition, on comparing these two, the film at 0.1M with TiCl₃ precursor has favorable microstructural characteristics than the other one. But the dislocation density is minimum for the film at 0.05M with TiAcAc precursor than the 0.1M with TiCl₃ precursor. The optical properties of semiconductors mainly depend on the structural disorder [16]. The film at 0.05M with TiAcAc precursor is having promising optical properties such as high band gap energy as 3.6eV, high refractive index, low extinction coefficient and high intense PL emission than the other films due to the minimum dislocation density. Furthermore, the film deposited for 0.05M for Titanyl acetylacetonate as precursor had appropriate characteristics, which make the optimized deposition as the most suitable for gas sensing and optoelectronic applications.

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