# Deposition of Doped $TiO_2$ Thin Film by Sol Gel Technique and its Characterization: A Review

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*Abstract*—**Titanium dioxide has wide area of applications ranging from CMOS to photocatalyst upto self cleaning glass and solar panels. The Sol-Gel spin coating technique is most attractive technique due to its so many advantages such as easy preparation method, less complicating instruments and less time consuming. The Sol-Gel spin coating was successfully used for doped $TiO_2$ thin films deposition on silicon wafer followed by annealing processes. $TiO_2$ thin films were deposited on silicon wafer using sol-gel technique. These deposited films can be characterized by various methods such as X-ray diffraction (XRD), surface profilometer, ellepsometer and ultraviolet visible spectroscopy. The XRD can be used to show the presence of anatase $TiO_2$ phase in the films deposited. The UV spectroscopy can be used to lookout the shifting of absorption edges of $TiO_2$ film towards visible light region which depends solely on doping concentration. The mechanism of depositing a thin film of $TiO_2$ with different doping materials with different concentration is discussed here in this paper.**

*Index Terms*—**Titanium dioxide ($TiO_2$) , Sol-gel, Doping, XRD, Grain size, Band gap, thin films.**

## I. Introduction

$TiO_2$ films are extensively studied because of its interesting chemical, electrical and optical properties. The interest in $TiO_2$ was mainly due to its non-toxicity and good stability in various environments [1]. $TiO_2$ is a high band gap semiconductor that is transparent to visible light and has excellent optical transmittance. The American Food and Drug Administration (FDA) has approved the use in human food, drugs and cosmetics and compounded in food contact materials such as cutting board and other surfaces in contact with unprotected food [2]. For photovoltaic applications, $TiO_2$ photo-catalyst is effective in solar light or light from visible region of the solar spectrum need to be developed as future generation photo-catalytic material [3].$TiO_2$ has high refractive index and good insulating properties, and as a result it is widely used as protective layer for very large scale integrated circuits and

for manufacture of optical elements. Such as dye-sensitized photovoltaic cells as well as antireflective coatings, gas sensors, electro-chromatic displays, and planar waveguides.

The main difficulty encountered with $TiO_2$ is the high recombination rate of the photo excited electron hole pairs in the irradiated particles [4]. This problem can be resolved by changing the structure of photo catalyst by doping with ion such as iron or other metal. However the doped $TiO_2$ films have shown potential for uses in number of electronic device applications. Additionally, good dispersibility of $TiO_2$ is very advantageous in enhancing their UV screening efficiency [5]. The high dielectric constant of $TiO_2$ allows its considerations an alternative to silicon dioxide for ultra thin gate oxide dielectrics used in memory and logic devices. The dielectric properties of $TiO_2$ have been of great interest for applications in the telecommunications industry due to its unusual high dielectric constant and low dielectric loss [6]. Doping $TiO_2$ with Pt, Fe or other metal ions shifts the threshold for photonic excitation towards the visible range [7]. Fe ions doped into $TiO_2$ have caused changes in phase composition and some properties of the catalyst such as phase composition, particle size and surface area [8].

Several methods have been used to prepare Titanium films, and these include chemical vapor deposition (CVD), pulsed laser deposition, reactive sputtering and sol-gel deposition. The sol-gel technique has emerged as one of the most promising techniques as this method produces samples with good homogeneity at low cost. The films deposited by this method results a film with high dielectric constant which is suitable for metal oxide semiconductor capacitor [9]. The sol-gel process is one of the most potential technologies for the preparation of $TiO_2$ photo catalyst [10]. The sol-gel process can be accomplished using different deposition routines. The preparation of $TiO_2$ thin films by spin coating of sol precursor onto microscopic glass slides, silicon and indium tin oxide (ITO) coated glass substrates has been recently reported. This method of film preparation is preferred to other sol-gel variants because of its compatibility with current practices of silicon technology. The material generally can be formulated in one of three main crystallographic phase's i.e rutile, anatase and brookite [11]. Chemical doping can also cause structure and morphology changes, for example it can force the transformation from the anatase to the rutile structure [12].The presence of anatase structure in Fe doped $TiO_2$ films were identified from the x-ray diffraction pattern. The electrical properties of the $TiO_2$ thin films were changed with the increasing of the annealing temperature [13].This paper mainly focuses on the results of morphological and

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structural analysis of thin nanocrystalline doped $TiO_2$ films using x-ray diffraction (XRD).

## II. Doping Materials and Preparation method

Most of the metals and non metals may be used as doping material. Generally the transitional elements are used for doping purposes. Table 1 provides the list of Doping material that can act as dopant.

### A. *Cerium Doped TiO2*

Sol-gel method may be used to prepare Cerium doped $TiO_2$ thin layer. Composition of various chemicals consist of tetrabutyl titanate, $Ce(NO_3)3{\cdot}6H_2O$ , absolute alcohol

TABLE I
Doping Elements

| Doped Element | Type of Dopant | Application |
|---|---|---|
| Pt | Metal | Gas Sensor |
| Cr | Metal | Gas Sensor |
| Fe | Metal | Photocatalyst |
| Zn | Metal | Photocatalyst |
| C | Non Metal | Waste water treatment |
| Ce | Metal | Electroluminescent devices |

(≥99.7%) and HCl [14]. The quantity of tetrabutyl titanate was 135 ml that is to be poured into 360 ml absolute alcohol and stirred continuously. Afterwards 11.8593 g $SnCl_2{\cdot}2H_2O$ was added to another 180 ml absolute alcohol solution with 1 vol.% of HCl was added to the solution to insure $SnCl_2{\cdot}2H_2O$ to be sufficiently dissolved. Then, both solutions were mixed and definite amounts of $Ce(NO_3)3{\cdot}6H_2O$ nitrites were respectively added and stirred to form Ce3+ doped sols.

### B. *Fe doped*

The substrate was firstly cleaned before deposition of thin film of Fe doped $TiO_2$. For this substrate such as glass or silica ring is to be kept in an oven for drying out the moisture around a temperature 130 degree celsius. Firstly the substrate was dipped in solution of titanium peroxide sol having the known concentration of Fe and PEG for 10–15 min. Then the sol attached to the substrate was allowed to dry at room temperature. A very thin and uniform film of titanium peroxide was formed on the substrate which must be dried in an oven at particular temperature for certain duration. A thin film of iron–titania (Fe–TiO2) was formed on these substrates [15].

### C. *Carbon doped*

The carbon doped $TiO_2$ thin layer was prepared by sol gel method. Firstly the $TiO_2$ solution is to be prepared by conventional sol gel method. The C-doped $TiO_2$ film was deposited by adding 1.0 g of $TiO_2$ and 0.5 g glucose into 70 ml of de-ionized water. Substrate must be cleaned before dipping into the mixture solution. Then the autoclave was maintained at 423 K for 12 h and air cooled to room temperature. The resulting C-doped $TiO_2$ film was collected and washed through with water and ethanol, and then calcination is done in the furnace at 373 K for 1 Hr. approximate[16]. The samples prepared were in three concentration including low concentration film, middle concentration film and high concentration film, respectively. The figure 1 shows the generalized step to be followed during sol gel preparation.

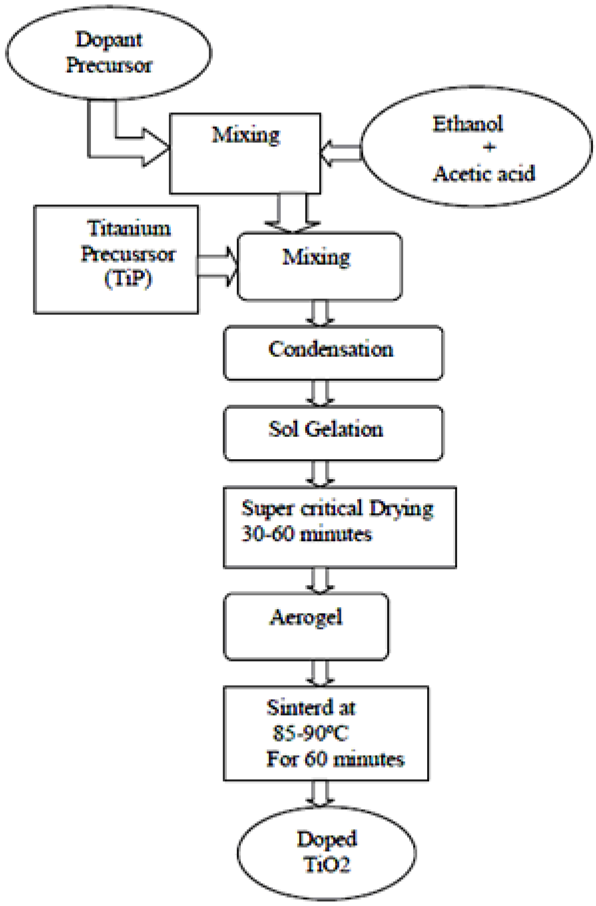


Fig. 1. Flow chart depicting the steps of sol gel process.

## III. Results and Discussions

Samples fabricated by sol gel technique can be characterized either by X-ray diffraction (XRD), surface profilometer, ellepsometer or ultraviolet visible spectroscopy or SEM. The XRD data usually in the form of XRD diffraction peak plotter as (2ɵ vs. intensity). XRD plot of Fe doped $TiO_2$ thin films deposited are shown in figure 2. The XRD exhibit different crystalline phase of Fe doped $TiO_2$ thin film were $TiO_2$ (101), $TiO_2$ (004), $TiO_2$ (105), $TiO_2$ (200), $TiO_2$ (204), and $TiO_2$ (211). Figure 3 shows the scanning electron microscopy (SEM), image of carbon doped $TiO_2$ film [15]. The SEM shows that the sample consists of large amounts of mono dispersed particulates with a size of around 5 nm, which is consistent with the XRD result. Besides, one can easily observe that the C-doped $TiO_2$ film is porous, while undoped $TiO_2$ film shows more agglomeration [16]. The porous structure has been shown to be very important for the photocatalytic activity of $TiO_2$ films due to its enhanced surface area.

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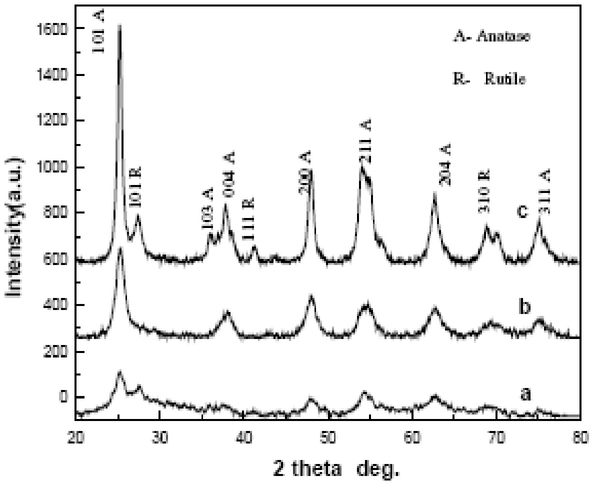


Fig. 2. XRD pattern of Fe doped $TiO_2$ [15]

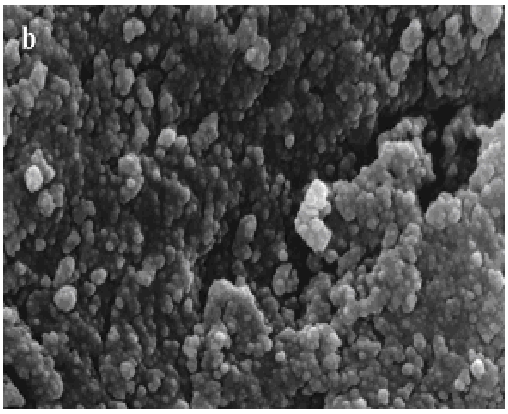


Fig. 3. SEM image of carbon Doped $TiO_2$ Film [14]

Figure 4 shows the optical transmittance spectra of $TiO_2$ and Fe doped $TiO_2$ films. The absorption edges of the Fe doped films are shifted to the longer wavelengths and show a clear dependence on the Fe concentration. Thus the Fe doping causes a red shift which in fact leads to more visible light absorption. It was assumed that the efficiency of metal doped $TiO_2$ under visible light strongly depend on the preparation method used. In same cases, such doped photo catalysts may show no activity or lower activity in the UV

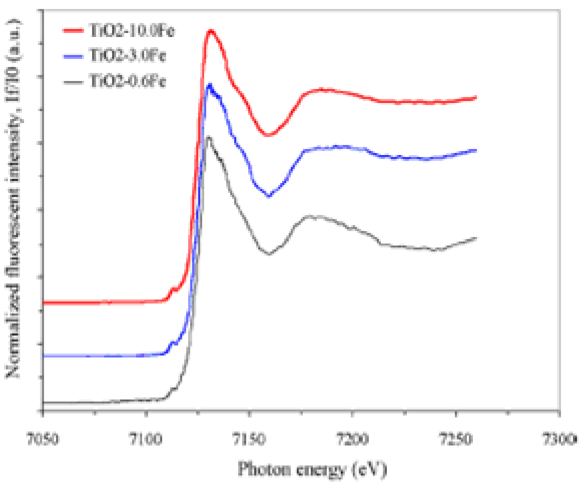


Fig. 4. Optical transmittance spectra of Fe doped $TiO_2$ Films [15]

spectral range because of higher carrier recombination rates through the metal ion levels. By increasing the concentration of Fe further the absorption edges was found to be shifted towards shorter wavelength.

Surface profilometers were used to measures surface profiles, surface roughness, surface thickness and other finish parameters. The surface thickness solely depends upon the concentration of sample. Experiments have showed that the thickness of sample 20mg, 40mg, 60 mg was found to be 1.67 µm, 4.6 µm, and 4.7 µm respectively. Ellepsometer was used to find the refractive index of the deposited thin films on the silicon wafer. The average refractive index for different concentrations is around 2.395.

## IV. Conclusion and Future Scope

In this work, we successfully focused on thin film deposition using sol gel techniques. The deposition was carried out with spin-coating process. The result by XRD pattern of $TiO_2$ thin film deposited on silicon wafer capable of describing the grain size of TiO2 as $TiO_2$ (101), $TiO_2$ (004), $TiO_2$ (105), $TiO_2$ (211), $TiO_2$ (204) respectively. Also one can observe the peak if it is present. The Films with Fe doping showed a better photo catalytical performance, so it can be used in photo-electrolysis for water splitting and in photo-catalysis for the degradation of organic pollutants. In some elements the band gap decreases with increase of doped element concentration as examined by researchers. The thin film deposited can be also used for fabrication of sensors.

Experimental results have been reported that the sensor response time that was related to the rate of change of the sensor resistance, can be controlled by the activation energy. It has been also observed that $Li^+$ doping in $ZrO_2$–$TiO_2$ enhances the humidity sensitivity by two orders of magnitude, and also improves the linearity of the characteristics. A major area of future research would be the development of new dopant, new method of dopant incorporation into $TiO_2$ structure as well as new application for environmental and gas sensing technology. The most important challenge which faces titania based catalysis is stable $TiO_2$ with predictable photo-activity in UV and visible light.

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