Yttrium Doped TiO$_2$ Thin Film for Gas sensing application Prepared by Spin Coating Method

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Abstract: Yttrium (Y) doped and pure Titanium Di-oxide (TiO$_2$) thin films were prepared by using spin coater. The coater was set up in laboratory with low cost investment. The films were calcined at 450°C for 1 hour. For characterization, Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Atomic Force Microscopy (AFM) were carried out. LCR Bridge - GW Instek LCR-821 was used for gas sensing applications. XPS showed that the change of electronic structure due to Y doping. SEM and AFM analysis were carried out to determine the surface morphology of the films. Yttrium (Y) decreased the crystallite size of the films and increased the surface roughness and porosity value, which was very good for many sensing applications. Gas sensing property of the deposited films were improved by the incorporation of yttrium impurities and the sensing property improved almost two times than pure TiO$_2$ thin film. Different researches have been done their research related to this topic but no one researchers provide a precise explanation of their results, authors of this research have tried to do that. Moreover the films were prepared by a simple spin coater to reduce the production cost also.

Keywords: thin film, crystal structure, surface roughness, extrinsic impurities.

1. Introduction

Our climate is getting poisoned by poisonous fumes day after day. It emerged from the functions of factories, internal combustion engines, etc. To control the air quality, Waste products should be controlled. If it is possible to control the pollution, than the toxicity in air will be decreased [1,2]. The universe is surrounded by dangerous and distinct poisonous gases, which can drive us to death in the future. We have a duty to maintain such gases in the environment.
A large number of workers died every year because of toxic gases who worked in mining plant, coal plant, septic tank and drainage system. The number of people who died while cleaning sewers and septic tanks in India increased by almost 62%, from 68 in 2018 to 110 in 2019 [3]. At least 592 workers were died across Bangladesh in 2018 [4]. So it is our responsibility to save the worker from toxic gases. In the market, gas sensors based huge technologies are available. Much effort has been made in recent years to boost the Gas sensors selectivity and responsiveness. TiO$_2$ has received attention and is given prime importance in gas sensor industry [5]. TiO$_2$ Chemical stability, non-toxic condition, low cost, production versatility, and ease of use of TiO$_2$ attract researchers [6]. All over the world a lot of techniques are developed to fabricate TiO$_2$ thin films as like as PLD (Pulsed Laser Deposition), Sol-Gel dip coating, CVD (Chemical Vapor Deposition), Evaporation, Sputtering etc. [7,8]. Spin coating technique has been used for its good quality film [8], the short coating time and high resist film [9], and a homemade spin coater can reduce the initial cost also. TiO$_2$ thin films can be obtained using the sol-gel technique, which is a reliable and low-cost chemical route too but the spin coating method is widely used for the deposition of materials [10].

TiO$_2$ is an n-type semiconductor with low conductivity [11]. There was a lot of effort there has been given for the doping of TiO$_2$ with metal atoms, where the electrons are transferred from one atom to another atom, allowing creatures to the total electrical charge to be generated [12]. Transition metal ions like Iron (Fe), Chromium (Cr), Cobalt (Co), yttrium (Y) etc. can be used as dopant in TiO$_2$ thin films [13].

The misfit strain energy formed from of Y$^{3+}$ (1.015Å) and Ti$^{4+}$ (0.68Å) in yttrium doped TiO$_2$ thin film [14]. In this research, Yttrium doped TiO$_2$ thin films were fabricated using a simple spin coater and investigated gas sensing properties, crystal structure, microstructure and optical properties. Because of size differences of Y$^{3+}$ and Ti$^{4+}$, substitution doping will be happened. The aim of this work was to find the optimum Yttrium doping concentration to enhance gas sensing properties and to find the structural, morphological and electron transportation ability of TiO$_2$ thin films on a glass substrate.
2. Methodology
Titanium isopropoxide (TTIP) (Sigma-Aldrich, 97%) was as a precursor of TiO$_2$, and ethanol (C$_2$H$_5$OH) was used as a solvent. The secondary solution of yttrium (III) nitrate hexahydrate (Y(NO$_3$)$_3$.6H$_2$O) was dopant precursor for Y$^{+3}$. The precursor and dopant precursor were mixed in different ratio to form 0%, 1%, 2%, and 3% Y doped TiO$_2$ thin film.
A simple spin coater was made in lab (Fig.S1), from locally available components. The thin films were prepared by using the homemade spin coater. The slide were spun in air at 2000 rpm for 1 minute and annealed at 450°C for 60 minutes. The XRD patterns of un-doped and Y doped TiO$_2$ thin films were analyzed by ‘Bruker, D8 Advanced’ machine, where the wavelength of X-ray radiation was 1.5406 Å for CuK$\alpha$. In this research, the films were characterized by SEM (ZEISS). The parameters of the SEM machine were fixed as: EHT- 20.00 KV; WD - 6.5; Mag.; 20 KX. For determining the surface roughness values, AFM analysis was carried out. XEI-70 AFM Software was used to analyses the images. XPS was used to find out to determine the position of dopant atom. Finally gas sensing properties were measured by using LCR Bridge-GW Instek LCR-82, where different gases (NH$_3$, C$_3$H$_8$O, CO and CO$_2$) were used for sensing application.

3. Results and Discussion
3.1 XRD analysis
Structural characterization of undoped and yttrium (Y) doped TiO$_2$ was obtained by X-ray diffraction. The stabilized Anatase tetragonal phase was found and dominant peaks were at plane angle 2θ=25.85°, 38.64° and 48.14° and the (hkl) coordinates were (101), (112), (200) which corresponded to ICSD file no. 98-015-4601, illustrated in Fig.1.

![X-ray diffraction patterns of pure and Y:TiO$_2$ thin films](image)

Fig.1: X-ray diffraction patterns of pure and Y:TiO$_2$ thin films
From that peak analysis it was found that the films were polycrystalline with tetragonal crystal structure, because nucleation sites started during sintering and films became more crystalline [15]. The crystallinity of the film influenced the transport properties of the photo generated electrons and holes to the film surface [16]. With increasing the dopant concentration, the peaks became wider and gradually removed. At Y=3% the additional peak (400) was raised which indicated the alteration of plan. The preferred orientation of the film was determined in texture coefficient \( T_c \) relation, which is shown in the following Eq. (1) [17].

\[
T_c (hkl) = \frac{\frac{I}{I_0}}{\frac{1}{n} \sum_{i=1}^{n} \frac{I}{I_0}} \quad (1)
\]

Where, where \( I \) was measured intensity, \( I_0 \) was JCPDS intensity and \( n \) was the reflection number. From that calculation (101) and (200) plan was indicated as preferred plan for TiO\(_2\) thin films.

An important scenario was observed that Y concentration shifted the peak (101) from right to left. The intensity of (101) diffraction peak decreased with increasing Y doping. The ionic radius of \( Y^{3+} \) was larger than \( Ti^{4+} \). Hence, \( Ti^{4+} \) was replaced by \( Y^{3+} \). There was on peak for \( Y_2O_3 \) which indicated that the proper doping process. \( Y^{3+} \) ions were not segregated to form \( Y_2O_3 \) at \( Y=0\% \), \( Y=1\% \) and \( Y=2\% \), but at \( Y=3\% \) a small amount of segregation was observed in morphological analysis (AFM and SEM). Due to doping of yttrium different structural changes were found. Those were calculated by using different techniques, among of them Scherrer formula was used to calculate lattice parameters, shown in Table 1. Lattice parameters were calculated by using the Scherrer Eq. (2) [18].

\[
d = \left( \frac{k\lambda}{\beta \cos \theta} \right) \quad (2)
\]

Where, \( \lambda \) (0.154 nm) was the wavelength of X-rays, \( \theta \) diffraction angle, and \( k = 0.9 \), \( \beta \) was full-width half maximum intensity (FWHM) of the diffraction peak.

The crystallite size decreased with increasing dopant. Crystallite size, lattice strain, and dislocation density are shown in Table S1. Due to Y doping, lattice parameters a, b and c axis, were changed. So, crystal structure changed, and derived a structural transformation (Tetragonal to orthorhombic) or (Anatase to Pseudobrookite). For 3%Y doping orthorhombic structure was formed i.e. Pseudobrookite but some Anatase also existed at that point shown in Table 1.
Using the following Eq. (3), the lattice constants were determined [16].

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2 + b^2 + c^2}$$  \hspace{1cm} (3)

The stability of the films depends on the stresses of the film. The stress ($\sigma$) of the prepared thin films were calculated using Eq. (4) [19].

$$\sigma = \frac{2C_{13} - C_{33}(C_{11} + C_{12})}{2C_{13}} \times \frac{(C - C_0)}{C_0}$$  \hspace{1cm} (4)

Where, $C_{11} = 208.8$ GPa, $C_{33} = 213.8$ GPa, $C_{12} = 119.7$ GPa and $C_{13} = 104.2$ GPa. The resultant stresses are shown in Table 1. From the XRD analysis, in terms of crystallite size, it is possible that $Y^{3+}$ ion doping promoted the anisotropic adsorption of ions on (101) planes of $\text{TiO}_2$, and thus enhanced the anisotropic growth of $\text{TiO}_2$ crystallites [20].

However, $Y=1\%$, $Y=2\%$, and $Y=3\%$ samples showed an increase in lattice parameters and decreased crystallite size which can be related to high lattice distortion in the crystallization process [21]. It was found that variation in ionic radius of Y and Ti changed the axis values and helped to separate the electrons or removed the possibility of recombination of hole and electron pairs [22]. As a result the sensitivity of thin films were increased.
3.2 Surface morphology

In this research, SEM images of the doped and undoped TiO$_2$ thin films are given in Fig. 2.

![SEM images of TiO$_2$ thin films](image)

Fig. 2: SEM images of TiO$_2$ thin films, (a) Pure TiO$_2$; (b) 1% Y:TiO$_2$; (c) 2% Y:TiO$_2$; (d) 3% Y:TiO$_2$.

It was found that the Y:TiO$_2$ films were porous as a result the reactive surface area of the films increased which was very important for gas sensing applications. The porosity of the films were increased with increasing the concentration of Y. at Y=2% highest amount of porosity was noticed. The pores were acted as conducting channel for gas sensing.

At Y=3% the porosity became decreased, it might be the effect of structural change which is shown in XRD analysis. The grain growth also happened in 3% Y:TiO$_2$ film (Fig. S2). The particles were in spherical in shape too. For determining the component, EDX & XPS were carried out (Fig. S3 and Fig. S4) of Y:TiO$_2$ film, which is shown in supplementary files. The element mapping established that the existence of Y in TiO$_2$ and Y$_2$Ti$_2$O$_7$ was formed [24]. The surface roughness values of TiO$_2$ and grain growth values of the films were determined from the AFM image analysis. AFM morphological images are shown in Fig. 3.
Fig. 3: AFM images of TiO$_2$ thin films, (a) Pure TiO$_2$; (b) 1%Y:TiO$_2$; (c) 2%Y:TiO$_2$; (d) 3%Y:TiO$_2$.

The formation of Anatase TiO$_2$ crystals increased the surface roughness and developed pores [25]. It was found that the grain sizes increased with increasing the dopant concentration and Fig.3 indicated that maximum rough surface was found at 2%Y: TiO$_2$. The minimum grain size was found 35 nm, when Y=0%, and maximum grain size was 48 nm when Y=3%. The roughness was maximum (S$_a$=116.39) when Y=2%. At 3%Y:TiO$_2$, the grain became enlarged and the roughness became low (S$_a$=78.85), all other roughness values are shown in Table 2. So, the less amount of reactivity of sensing for gases was found.

| Sample % | Grain size (nm) | Roughness |
|----------|----------------|-----------|
|          |                | S$_a$ | S$_q$ | S$_z$ |
| Y=0      | 35             | 47.17 | 94.70 | 458.3 |
| Y=1      | 42             | 56.40 | 103.33 | 644.6 |
| Y=2      | 43             | 116.39 | 198.49 | 750.6 |
| Y=3      | 48             | 78.85 | 110.04 | 622.56 |

3.3 Gas sensation

The operation temperature was 250$^\circ$C, which was fixed. The gas-sensing performance of the nanostructured thin films was tested using static gas-sensing system [26]. The reading was collected from the digital display and recorded before and after testing. The test was carried out by using NH$_3$, CO, CO$_2$, C$_3$H$_8$O and the concentration was varied from 100 to 900 ppm. The response (S) of the films to gas was calculated by using the following Eq. (5) [27].
\[ S = \frac{R_0 - R_G}{R_G} \]  

(5)

Where, \( R_0 \) was the resistance of air and \( R_G \) was the resistance of gas inside chamber. The sensing properties of any materials depends on crystallite size, reactive surface area, microstructure, structure, and grain sizes. At low temperature (<300ºC), oxygen was adsorbed on the oxide crystals surface as ions were formed by abstracting free electrons from the semiconductor solid, reducing the electrical conductivity[28].

A layer of oxygen ions that produced a repulsion force over the charge carriers inside the films. Then, in the middle of the crystals, the charge carriers were trapped and a leakage surface layer just below the crystal surface was formed. So, a potential barrier appears between the oxide crystals, causing an additional reduction of the electrical conductivity [29].

It was found that the response of films was increased with increasing concentration of NH\(_3\). At 300 ppm, the response was highest and 400 ppm to 900 ppm the response became constant. The response also related to the concentration of Y. At Y=0% the response was lowest and maximum response was found at Y=2%, after that the response decreased at Y=3%. Based on that, the additive of yttrium improved their sensing performance by the way of high surface area to volume ratio [30]. In the exposure of NH\(_3\), the gas reacted with the adsorbed oxygen, left free electrons and the formed ions kept free. The reaction can be represented as following Eq. (6) [31].

\[
\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O} + e^- \]  

(6)

The responses of different gases are given in Fig.4. All the responses of NH\(_3\) (a), CO (b), C\(_3\)H\(_8\)O (c), and CO\(_2\) (d) showed the concentration effect of yttrium and gases. But the percentages of response of NH\(_3\) was highest (a) and C\(_3\)H\(_8\)O was lowest (c).
Fig. 4: Response of different gases with different composition of thin films and concentrations of gases

The gases on the surface of the films conducted electrons. As a result the sensational properties were found. All the response percentages were found between 100 ppm to 200 ppm concentration, except C$_3$H$_8$O. The response percentages were increased with the increased of Yttrium (up to Y=2%), but at Y=3% the response became low but not less than 1% Y doped thin film. This statement was true for all kind of gases showed in the Fig. 4. This was happened, because of grain growth, low porosity, low surface roughness, structural alteration and agglomeration of yttrium on the surfaces of the films at 3% Y:TiO$_2$.

4. Conclusion

TiO$_2$ and Y:TiO$_2$ thin films were successfully fabricated by using spin coating technique. The films were sensitive for NH$_3$, CO, CO$_2$ and C$_3$H$_8$O gases. The films showed maximum
sensitivity for 2%Y:TiO$_2$ composition. The crystallite sizes of the films were decreased with increasing the Y concentration. The sensitivity of the films depended on surface porosity and surface roughness. Yttrium doped TiO$_2$ thin films, fabricated by spin coating method can be used in ceramic sensors of gas sensing applications.

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6. Supplementary materials
This paper contains supplementary material available online.

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