

THIN FILM OF TITANIUM DIOXIDE (TiO₂) USING SPRAY PYROLYSIS METHOD WITH APPLICATION OF LPG GAS

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ABSTRACT: Metal oxide semiconductors are device used as a gas sensor to detect the gases in an environment. They are widely used for safety because, many harmful gases present in environment. TiO₂ have better stability and remarkable properties as compared to other materials. TiO₂ is used for anticorrosion, self-cleaning coating, paints to solar cells, and photo catalysts. The properties of thin film strongly depends on method of deposition and chosen conditions such as annealing temperature, film thickness, nature of crystalline, grain size, morphology, ion bombardment during deposition technique, impurity etc. The process of deposition of thin film such as CSD or CBD ,spin coating, dip coating chemical vapour deposition(CVD),plasma enhanced CVD ,Atomic layer deposition, successive ionic layer adsorption and reaction(SILAR),electro deposition, spray pyrolysis etc.

In this article we concentrated on spray pyrolysis technique which is the most promising method on large scale productivity. Spray pyrolysis is a chemical method which uses liquid precursor solution for film coating. TiO₂ semiconductor metal oxide have been characterized using X-ray diffraction (XRD), Scanning electron microscopy (SEM),Transmission electron microscope (TEM),Atomic force microscopy etc. TiO₂ thin films has better selectivity and sensitivity to act as a gas sensor.

Keywords: Titanium Dioxide thin films, Deposition technique, XRD, SEM etc.

1. Introduction

Today we are using different types of sensor devices for detecting physical, chemical and biological signals to be measured and recorded. Thin films of metal oxide semiconductors are widely used as many applications. In Recent technology lots of industries has developed their fabrication units with utilization of nanomaterials. There are many ways to fabricate thin films depending upon type of applications. Thin films deposited by wide range of varying their application with forms of chemical compositions [1].Titanium dioxide also called as titanium (IV) Oxide or Titania and naturally occurring oxide of titanium, its chemical formula is TiO₂.Generally, it is sourced from ilmenite, rutile and anatase [2].

TiO₂ powder is a fine, white powder provides a bright and white pigment. Titanium dioxide has been used in industry and consumer products including paints ,coating, adhesives ,paper, plastics and rubber, printing inks, coated fabrics and textiles as well as ceramics, floor covering roofing materials, cosmetics,toothpaste,soap,water treatments agent pharmaceuticals

food colorants, automotive products, sunscreen, and catalysts [3].TiO₂ is a transition metal oxide therefore remarkable optical and electronic properties in applications with solar cell, gas sensor and photo catalysts. Semiconductor metal oxide like TiO₂, SnO₂, ZnO etc. are present.

Titanium dioxide exists in many polymorphs. Among them Anatase, rutile, and Brookite and its Density 3.895, 4.2743 and 4.123[4].These phases are characterized with high refractive index (anatase=2.488, rutile=2.609, brookite=2.583), low absorption and low dispersion [5].

2. Experimental

Spray Chemical Pyrolysis has been used to produce high purity, high performance and desired deposition on glass substrates to produce thin film of TiO₂.The pure TiO₂ thin films is successfully deposited by spraying 0.1M titanium trichloride solution on the glass substrate.

The electrical resistances, temperature coefficient of resistance and activation energy of the films has been calculated by measuring DC sheet resistance of the films at different temperatures with the help of static gas sensing system.

The XRD analysis of the prepared sample of TiO₂ thin film is done by using a BRUKER D8 ADVANCE diffractometer; Cu-K α X-rays of wavelength(λ)=1.5406Å and data taken by 2 θ range of 20 ° to 80° and surface morphology was studied using scanning electron microscopy (SEM) with a JEOL-540LV microscope.

3. RESULTS AND DISCUSSION

3.1 X ray Diffractometer

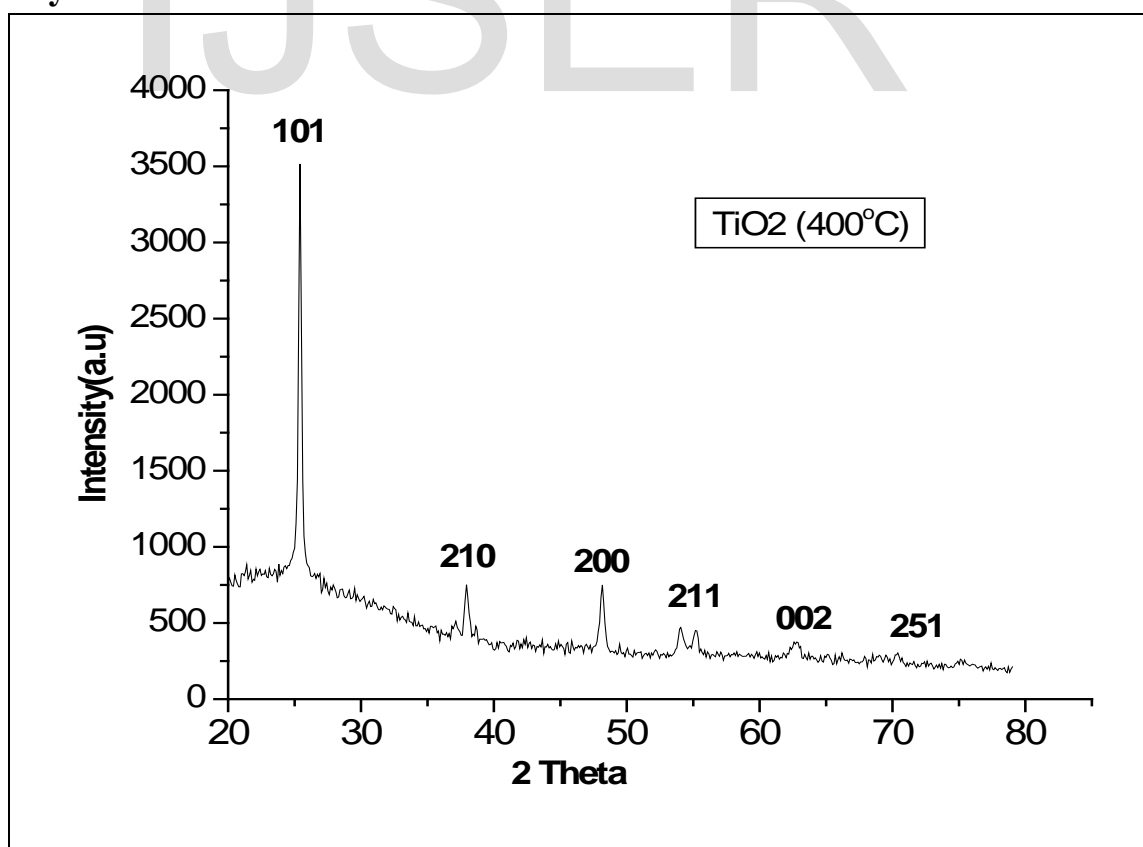


Fig 1.XRD Pattern of TiO₂ thin film

Figure 1 shows the XRD spectra of the TiO₂ films, as deposited, after annealing at 400°C for 2hrs, the films are in anatase crystalline phase with a preferential orientation of (101),(210), (200) and (211) peaks also appeared .The peak confirms its anatase structure. The XRD pattern agrees with JCPDS card no.21-1272(anatase TiO₂) [6].

Table 1.XRD data of TiO₂ thin film

| 2θ | θ | Cos θ | Sin θ | FWHM(°) | FWHM Radian | βcosθ | Size | d-spacing |
|-------|-------|--------|--------|---------|-------------|----------|------|-----------|
| 25.41 | 12.71 | 0.9776 | 0.2200 | 0.4008 | 0.006995 | 0.006838 | 21 | 3.5013 |
| 37.92 | 18.96 | 0.9457 | 0.3249 | 0.4008 | 0.006995 | 0.006615 | 21 | 2.3709 |
| 48.14 | 24.07 | 0.9130 | 0.4079 | 0.4008 | 0.006995 | 0.006386 | 22 | 1.8885 |
| 54.08 | 27.04 | 0.8907 | 0.4546 | 0.6012 | 0.0104929 | 0.009346 | 15 | 1.6945 |
| 55.16 | 27.58 | 0.8864 | 0.4630 | 0.6012 | 0.0104929 | 0.09301 | 15 | 1.6637 |
| 62.72 | 31.36 | 0.8539 | 0.5204 | 0.8016 | 0.0139905 | 0.011946 | 12 | 1.4802 |
| 70.41 | 35.21 | 0.8170 | 0.5766 | 0.4008 | 0.006995 | 0.005715 | 25 | 1.3359 |

The average particle size has been calculated by using the Debye-Scherrer formula.

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

Where D is the mean size of crystallites(Particle Diameter in nm), K is crystallite shape factor a good approximation is 0.9, λ is the X-ray wavelength(0.1540nm),β is the full width at half the maximum (FWHM) in radians of the X-ray diffraction peak and θ is the Bragg's angle (deg.)

$$D = \frac{0.9 \lambda}{(\beta \cos \theta)} \dots\dots\dots (2)$$

Bragg's Law refers to the simple equation:

$$n\lambda = 2d \sin\theta \dots\dots\dots (3)$$

Order of Reflection (n) × Wavelength (λ) = 2 × Interplanar spacing (d) × Sinθ

So, interplanar spacing can be calculated easily from the formula as:

Interplanar spacing (d) = Order of Reflection (n) × Wavelength (λ) / 2 × Sinθ

Default value of wavelength (λ) of LASER is set to 0.15406nm, which is mostly used in the instruments and Order of Reflection (n) is 1, which is depends on how the width (0.94-spherical and 0.89-integral breadth of spherical crystals is round up 1) [7].

The instrumental broadening is generally done while determining average particle sizes which is less than 100nm. Instrumental broadening formula can be used only if strain and other sources of broadening are small.

The sample broadening is described by

$$FW(S) \times \cos\theta = \frac{K + \lambda}{Size} + 4 \times \text{Strain} \times \sin\theta \dots\dots\dots(4)$$

The total broadening is described by

$$\beta t^2 \approx \left\{ \frac{0.9\lambda}{D \cos\theta} \right\}^2 + \{4 \varepsilon \tan \theta\}^2 + \beta_0^2 \dots\dots\dots(5)$$

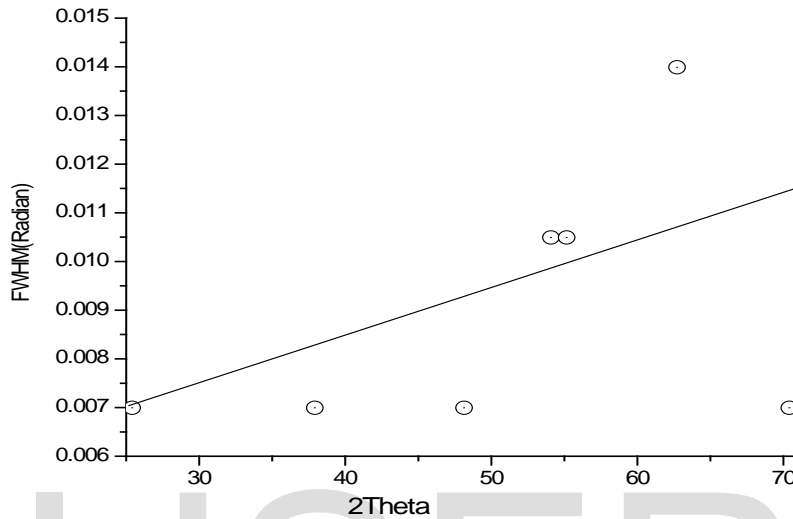


Fig. 2 Plot of the peak widths (FWHM) for TiO₂ thin film at various diffraction angle.

Using of a least squares fit, the particle size and strain can be calculated. Williamson-Hall gives the crystallite size and the strain. W-H plotted with $\sin\theta$ on x and $\beta\cos\theta$ on y axis (in radian) the slope of the fitted line gives you the crystallite size and the intercept gives you the strain.

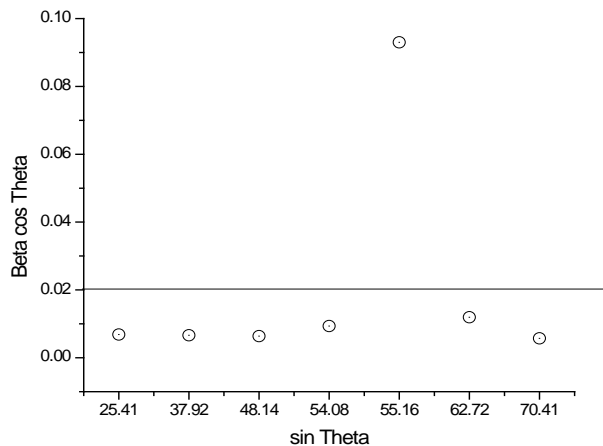


Fig.3. Williamson Hall Plot –TiO₂ thin film

Specific surface area describes the properties of the material, type and structure of the materials. SSA can be calculated using formula

$$SSA = \frac{SA_d}{V_d \times (\text{density})} \dots\dots\dots (6)$$

$$S = \frac{6 \times 10^3}{D \times \rho} \dots\dots\dots (7)$$

Where, SSA is Surface Area per mass, V_d is domain volume, SA_d is surface area, D is the size of the particle and ρ is the density of the TiO_2 .

Table.2. SSA of Thin film TiO_2

| Particle Size(nm) | Surface Area (nm ²) | Volume (nm ³) | Density g.cm ⁻³ | SSA (m ² .g ⁻¹) | S A to Volume Ratio |
|-------------------|---------------------------------|---------------------------|----------------------------|--|---------------------|
| 19 | 1133.54 | 3589.54 | 4.23 g/cm ³ | 4.23 | 0.32 |

3.2. Scanning Electron Microscopy Analysis of TiO_2 thin film

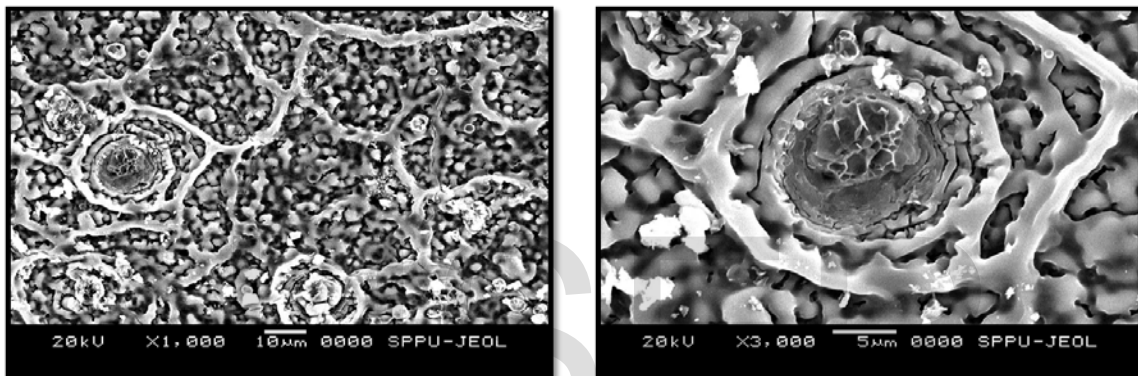


Fig.4.SEM of TiO_2 thin film sample at 400°C

A Scanning Electron Microscopy SEM [Model SPPU- JEOL 6300] is used for the study of microstructure as well as morphology of the thin film of TiO_2 . In this, film structure is like a web morphology. This images is recorded at X1000 and X3000 magnification [8].

3.3 Electrical Properties

3.3.1 Resistance of the TiO_2 thin film

The resistance of the film is measured using half bridge method with the help of static gas system. We observed that if temperature increases, resistance decreases due to increasing drift mobility of charge carriers and at certain level steady the resistance. Initially at Room temperatures it has no charge carriers and hence resistivity is high and at higher temperatures, a semi-conductor of valence electrons are free and is equal to conduction electrons that’s why resistivity decreases[10,11].

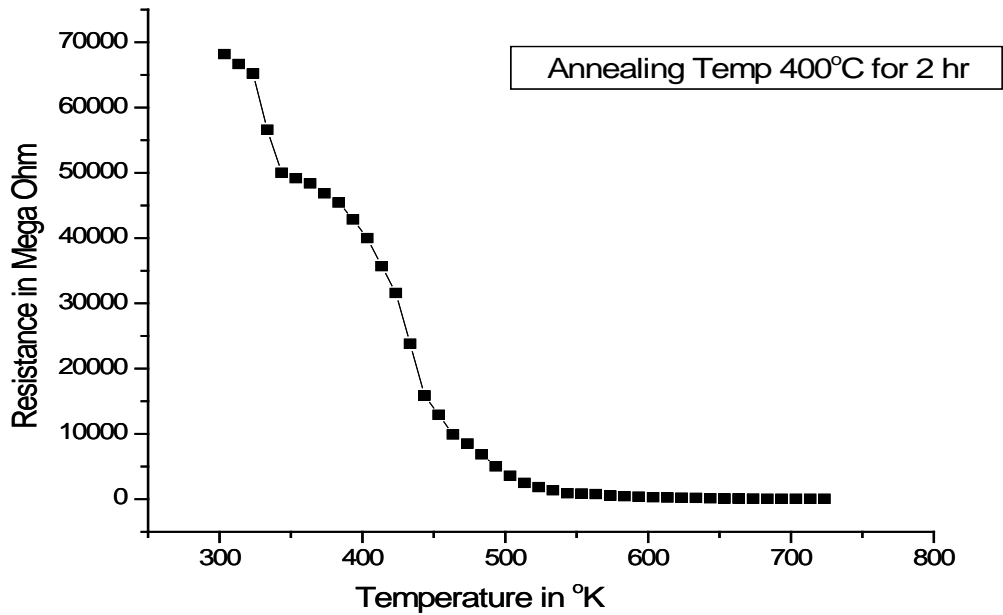


Fig.5. Temperature Versus Resistance of TiO₂ thin film at 400°C

3.3.2 .Activation Energy of the TiO₂ thin Film

Arrhenius plot shows the log R versus reciprocal of temperature (1/T) plot TiO₂ thin film. The temperature dependence of electrical conductivity(R) of TiO₂ thin film follows the Arrhenius equation is given by

$$R = R_0 e^{-\Delta E / KT} \dots\dots\dots (8)$$

Where R₀ is the resistance at room temperature, ΔE is the activation energy of the electrical conduction, K is the Boltzmann constant and T is the absolute temperature.

The activation energy has been determined by plotting graph between log R versus 1000/T (°K).It is found that the activation energy of TiO₂ thin film is 1.60eV[12].

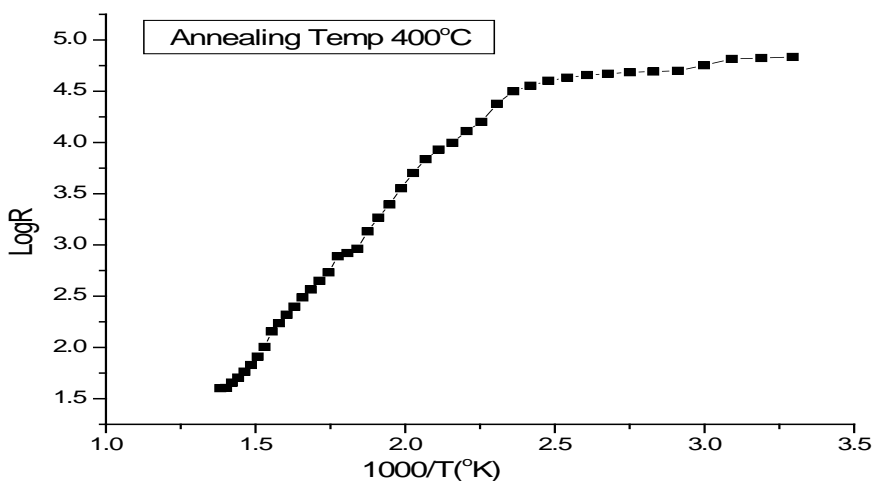


Fig.6.Variation of log R versus 1000/T for TiO₂ thin film.

3.3.3. Temperature Coefficient of TiO₂ Thin Film

With the help activation energies, the temperature coefficient of resistivity (TCR) can be obtained and TCR is most important parameters for characterizing the detectivity of sensors, it is defined as,

$$TCR = \frac{1}{R_0} \left(\frac{\Delta R}{\Delta T} \right) \dots \dots \dots (9)$$

Where, $\Delta R = R_2 - R_1$, R_1 in ohms at room temperature, R_2 is resistance in ohms at operating temperature and $\Delta T = T_2 - T_1$, T_1 is the room temperature in °C and T_2 is the operating temperature in °C.

The way to measure TCR is standardized in MIL-STD-202 Method 304. With this method, TCR is calculated for the range between -55°C and 25°C and between 25°C and 125°C. TCR depend on purity and temperature. TCR value of TiO₂ thin film nearly goes to zero, TCR may be positive, negative or stable value [14].

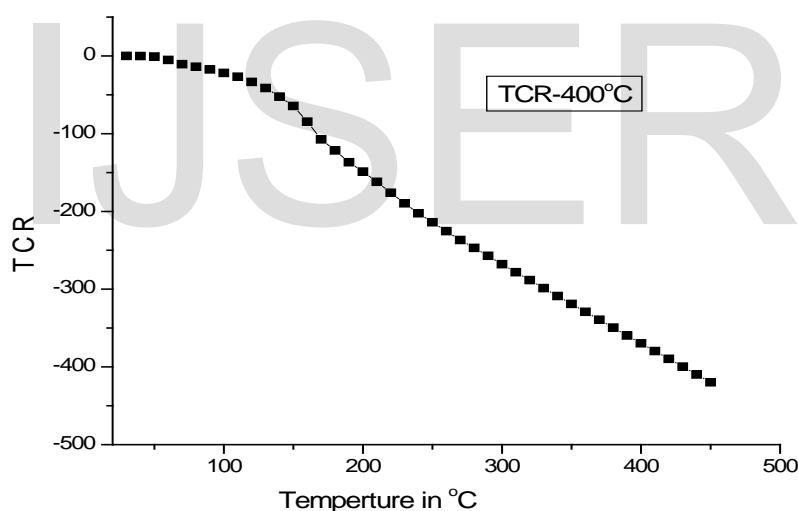


Fig.7. Activation Energy versus Temperature

4. Sensitivity of LPG Gas with different Operating Temperature

Gas sensing will be depend on which material doped, thickness of film, deposition technique, annealing temperature. The detection principle of metal oxide sensors is based on change of the film resistance due to adsorption of the gas molecules on the surface of a semiconductor. Anatase phase having stable transition state, this phase is used in many application like solar cell, gas sensor due to its higher photocatalytic activity [15].

The most important parameters of gas sensor are Sensitivity, Selectivity and Stability, Detection limit, Dynamic range, Linearity, Resolution, Response time, Recovery time, working temperature and Hysteresis Life cycle. All are used to characterize the properties of a particular material or device. An ideal sensor would possess high sensitivity,

dynamic range, selectivity and stability, low detection limit, good linearity, small hysteresis and response time and long life cycle [16]. We find characteristics of sensitivity, Selectivity and Response time in static measurement system. The varying sensitivity with temperature by taking 1000ppm of LPG gas. Therefore 350°C is optimal temperature for LPG gas.

Sensitivity can be determined by equation [10]

$$S = \left| \frac{R_a - R_g}{R_a} \right| \dots\dots\dots (10)$$

Where, Ra-Resistance of thin film in air atmosphere, Rg-Resistance of thin film in gaseous atmosphere.

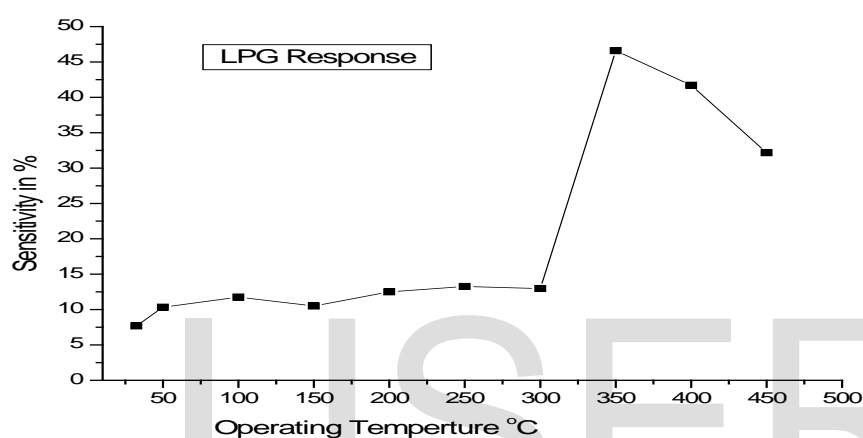


Fig.8.Sensitivity of LPG Gas

CONCLUSION

We have successfully fabricated pure TiO₂ thin film on glass substrate and studied structural, physical and electrical characterization. It was also found that the certain properties of gas sensing mechanisms for operating particular temperature.

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References

1. Liam Critchley. The use of thin films in sensors
2. <http://en.m.wikipedia.org/wiki/Titaniumdioxide> [Accessed: 3rd Feb 2019]
3. <http://www.chemicalsafetyfacts.org> [Accessed: March 11th 2019].
4. Tong Zhu, Shang-Peng Gao. The stability, electronic structure and optical Property of TiO₂ polymorphs. Department of Materials Science.

5. Thirugnanasambandan Theivasanthi and Marimuthu Alagar. Titanium dioxide Nanoparticles-XRD Analyses-An Insight
6. Antic Z, Krsmanovic RM, Nikolic MG, Cincovic MM, Mitric M, Polizzi S, Dramicannin MD. Multisite luminescence of rare earth doped TiO₂ anatase nanoparticles. *Mat.Chem Phys.* 2012; 135:1064-1069.
7. JI Langford and AJC Wilson, "Scherrer after sixty years: A survey and some new results in the determination of crystallite size," *J. Appl. Cryst.* 11 (1978) p102-113.
8. More AM, Gunjekar JL, Lokhande CD. Liquefied petroleum gas (LPG) sensor properties of interconnected web-like structured sprayed TiO₂ films, *Sensors and Actuators B* 129 (2008) 671–677
9. Fukushima, K., & Yamada, I. (1989). Electrical properties of TiO₂ films deposited by a reactive-ionized cluster beam. *Journal of Applied Physics*, 65(2), 619–623. doi:10.1063/1.343093
10. R. Y. Borse, A. S. Garde, *Indian J. Phys.* 82(10), 1319 (2008).
11. D. Patranobis, *Sensors & Transducers e Book (PHI)*, (2000)
12. D. Patidar* , K. S. Rathore, N. S. Saxena, Kananbala Sharma, T. P. Sharma ENERGY BAND GAP AND CONDUCTIVITY MEASUREMENT OF CdSe THIN FILMS Semiconductor and Polymer Science Laboratory, 5-6, Vigyan Bhawan, Department of Physics, University of Rajasthan, Jaipur-302004 (India), Ph./Fax: +91-141-2704056.
13. Yongfeng Ju, Mahua Wang, Yunlong Wang, Shihu Wang, and Chengfang Fu Electrical Properties of Amorphous Titanium Oxide Thin Films for Bolometric Application Hindawi Publishing Corporation *Advances in Condensed Matter Physics* Volume 2013, Article ID 365475, 5 pages <http://dx.doi.org/10.1155/2013/365475>
14. <http://www.resistorguide.com/temperature-coefficient-of-resistance/>
15. Jaya Bharathi J, N Pappayee Titanium dioxide (TiO₂) thin film based gas sensors, National Conference on Green Engineering and Technologies for Sustainable Future-2014 *Journal of Chemical and Pharmaceutical Sciences* ISSN: 0974-2115
16. V.E. Bochenkov, G. B. Sergeev Sensitivity, Selectivity, and Stability of Gas-Sensitive Metal-Oxide Nanostructures Laboratory of Low Temperature Chemistry, Department of Chemistry, M. V. Lomonosov Moscow State University, Moscow 119991, Russia