SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED TITANIA FOR GAS SENSOR APPLICATIONS

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SUMMARY

A gas sensor is a chemical sensor which provides an electrical output in response to the chemical collaborations with gas species only. It is commonly used for industrial applications where many gas storage containers are in use. In the industrial application gas sensors are used to determine gas leaks in order to prevent any harm to human health as well as to defend from any explosions that caused by leakage.

From the literature, it is observed that currently available sensors have two major inadequacies i.e. low sensitivity and high operating temperature [1]. We have to compromise with either sensitivity or operating temperature. A high sensitive gas sensor mostly works at a very high operating temperature which increases the power consumption. LPG is most harmful gas for its inflammable and explosive nature which gives many hazards to human and environment. The LPG sensor has become a very interesting topic in view of the fundamental research as well as industrial applications [2-3].

The growth of portable LPG sensors that are robust, tiny sized, long lifetime, quick response and have sufficient sensitivity to the ambient environment is necessary and demanded in order to prevent the explosion accidents in homes and industries for safety requirements. Solid-state LPG sensors of metal oxide are the most auspicious for the detection of LPG because of their solid structure, high selectivity, low price, and the ability of continuous monitoring [4]. The need for reliable, cheap and user-friendly gas sensors for the detection of LPG is industrially important and has led to a considerable expansion in the field of sensor research and development. The performances will be enhanced intensely by approving preparation conditions and by controlling deposition process. Numerous types of LPG sensors such as chemical sensors, the resistive and conductive type sensors using semiconductors and sensors based on metal polymer complexes have been investigated by different research groups in the world. So, a great attention has been recently remunerated to

the development of new material at the nano-scale.

Nanomaterials can enhance the performance of LPG sensor due to their much higher surface-to-volume ratio as compared to micro-size materials. To enhance the sensitivity verified by the nanostructured material based sensors, it gives a quick response. Grain size and porous structure have large effect on the gas-sensing properties of crystalline materials and their full characterization is the beginning of the study of materials [5].

Use of nanoscience and nanotechnology in manufacturing materials for sensor applications may improve the detection limit of gas sensors at lower temperatures. It is due to alterations of the space charge layers for each grain and improving other electronic properties of the material. The large surface to volume ratio of nanomaterials can be used for improvement in gas sensor development. The surface reaction is improved by the increase in the number of defect sites for the reaction. It will increase the sensitivity of the gas sensor.

The one-dimensional nanostructure with high aspect ratios makes it attractive in gas sensor production [6]. The space charge layer control of nanostructures make motivating since conduction can modify drastically with expansion and contraction of the layer in the presence of different gases. In sensing process, high non-equilibrium amount of oxygen vacancies in the oxide sensor material is important in achieving the goal, which would help to contribute in more effective movement of charge across the sensor material. At low operating temperature, the non-equilibrium exists and number of vacancies cannot be predicted. In next step, increasing the number of surface sites for gas interaction will help for detection of gas at room temperature. Further, the sensor material in modification of the space charge layer can be done by:

(i) Reducing the crystallite size,

(ii) Changing the defect chemistry within the space charge layer and surface of the material,

(iii) Changing the particle shape

Another motivating aspect of nanomaterials that makes it an interesting candidate for room temperature gas sensor which is because of the changes in the band gap reported at small sizes [7]. The band gap may be improved by changing the potential barrier energy required for charged species to conduct. Another enhanced feature of nanocrystallites is the conduction of electrons from the surface reaction. This conduction of electrons has to overcome a potential barrier induced by the space charge layer.

Even after half a century of research investigations on the fundamental properties of TiO_2 crystal phases remain a significant characteristic due to its important function to be successfully utilized as gas sensor and solar cell. The gap between valence and conduction bands and the optical absorption property are dynamic to all these applications. TiO_2 is an important metal oxide for broad range of gas sensing applications, because of its surface chemistry, charge transport and electrical properties. It is a versatile material widely used in industry, research and ecological cleaning. The bulk structure of titanium dioxide materials can exist in one of the three forms: rutile, anatase and brookite, rutile and anatase structure is shown in Figure 1. Each phase has its own structure along with a particular application [8-10]. TiO_2 is a versatile functional material due to its many unusual properties such as high refractive index, hydrophilicity [11], biocompatibility [12], semiconductivity, corrosion resistance, low cost, wide availability, nontoxicity and physicochemically stable nature [13] and also known for its gas sensing behavior [14-15]. Titanium dioxide has received considerable attention because of its excellent optical, electrical, mechanical, and catalytic properties, which makes it technologically useful. Its superior properties are due to chemical and biological inertness, non-toxicity, strong oxidizing/reducing power, cost-effectiveness and long-term stability against photo corrosion and chemical corrosion. The band gap of titania is about 3.2 eV. The band gap further increases with decreasing the particle size and hence the utilization typically confined within the UV-radiation of electromagnetic spectrum.

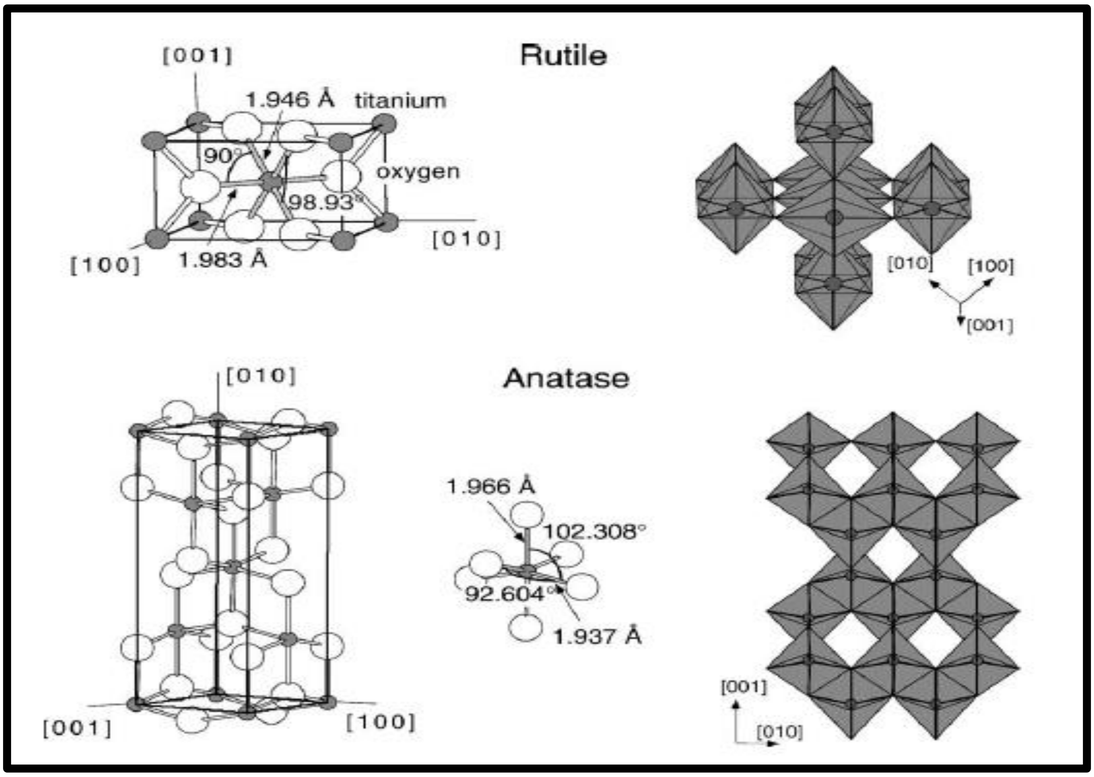

Figure 1: Bulk structure of rutile and anatase titanium dioxide showing the bond lengths and angles between atoms.

Basic requirement for the sensor is the change in electrical conductivity with exposure of LPG to surface of semiconducting oxides which depends on their band gaps, surface morphology, size, diffusion rate of gas and specific surface area. The semi-conducting properties of metal oxides represent the basis for their use as gas sensors, since the number of free charge carriers within the metal oxide and thus its electrical conductivity reversibly depends on the interactions with the ambient gas atmosphere.

Since the LPG sensing mechanism is based on the chemisorption reaction that takes place at the surface of the metal oxide. Thus increasing specific surface area of the sensing film leads to more sites for adsorption of surrounding gases. The oxygen adsorbed on the surface of the film influences the resistance of the titania based sensor. Initially oxygen from the atmosphere adsorbs on the surface of the film and extracts electrons from its conduction bands to form O_2^- species on the surface, consequently resistance decreases. After that an equilibrium state is achieved between oxygen of TiO_2 and atmospheric oxygen.

Use of nanotechnology in engineering materials for sensor applications may improve the working detection limit of gas sensors to lower temperatures. This will be achieved predominantly by alterations of the space charge layers for each grain and enhancing other electronic properties of the material. The large surface to volume ratio of nanomaterials can be used as an advantage to contribute in gas sensor development. The surface reaction on the gas sensor is improved when the number of defect sites for reaction is increased. The large surface area to volume ratio of nanocrystalline structures increases the opportunity for this surface reaction to occur. This in turn will increase the sensitivity of the gas sensor. The surface of nanomaterials can comprise much of the actual material making them ideal for gas sensors.

The additives in metal oxide are chosen for improving the interactions among the gas species and the sensing surface. A study of synthesis, characterization and LPG sensing properties of titanium oxide, PANI-TiO_2, Zn-TiO_2, and Ag-TiO_2 is summarized here:

Chapter 2 includes the gas sensing of titania based nanostructured materials. Liquefied petroleum gas is an inflammable mixture of hydrocarbon gases used as a fuel in heating utilizations and vehicles. The structural, morphological and optical properties of the prepared sensor structure have been studied by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and UV-Visible spectroscopy respectively. XRD revealed the crystallite size as 7 nm. SEM showed the regular and porous grape-like surface morphology before exposure to the LPG. The band gap of the material was found as 3.65 eV. The maximum sensing response was found as 1.34 for the exposure of 4% vol. of LPG and results were found reproducible. Figure 2 shows the lab model of experimental set-up for LPG sensing.

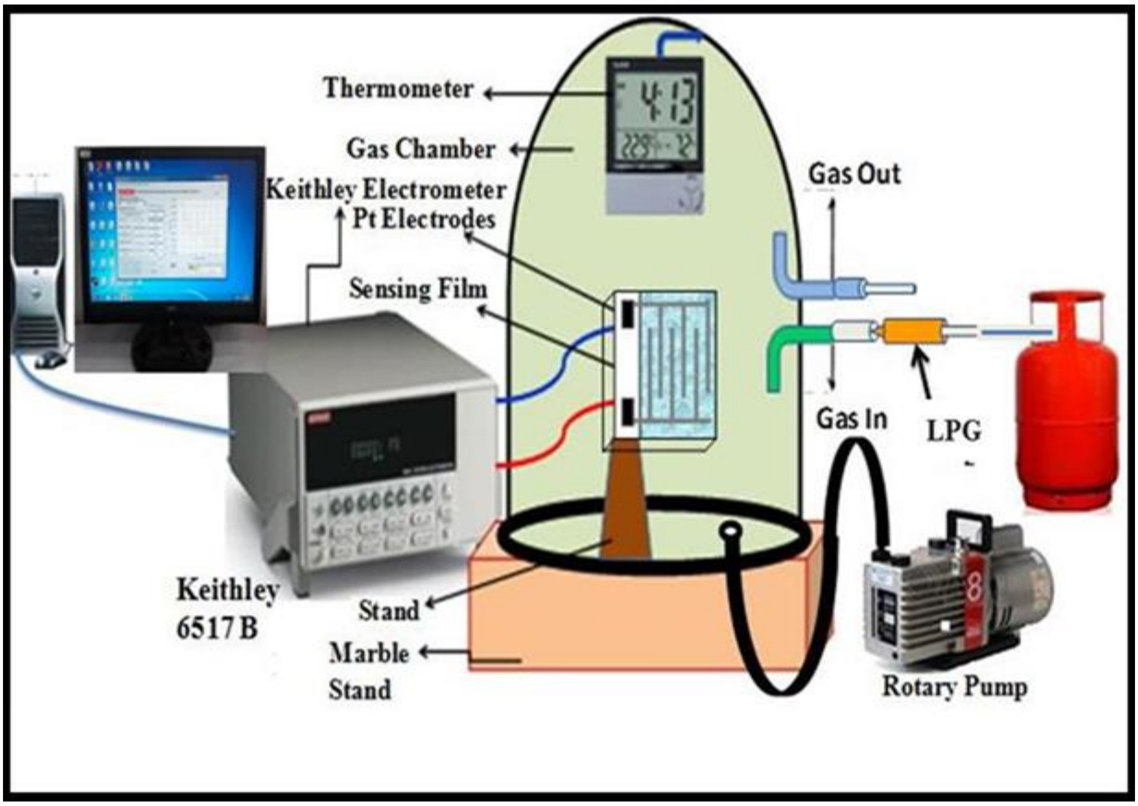

Figure 2. Gas sensing Set-up: Lab Model

Chapter 3 reports the utility of PANI doped titanium dioxide thin film on corning substrate with Inter Digital Electrodes (IDEs) prepared by spin coating technique as for LPG and CO_2 sensing. The increasing needs of carbon dioxide detection in various fields like air quality control, greenhouse monitoring and bio-related processes have been demanding high-quality CO_2 sensors in day to day. Optical properties were investigated using UV–Vis absorption spectroscopy. The surface morphology and structure of synthesised material were characterised by TEM and XRD analysis, respectively. The structural analysis confirmed the formation of PANI-TiO_2 having an average crystallite size 7 nm. The schematic of sensing mechanism and characteristics is shown in Figure 3. Variations in resistance with exposure of LPG to the sensing element were observed. Sensor response (S) as a function of time was calculated and its maximum value was found as 2.77 towards 2000 ppm of LPG, response time of the sensor was 156 s and recovery time was 140 s. Similarly, the sensor response (S) as a function of time was calculated and its maximum value was found as 53 for 1000 ppm of

CO_2. Response and recovery times of the sensor were observed as 9.2 min and 5.7 min respectively. The sensor was quite sensitive and results were found reproducible.

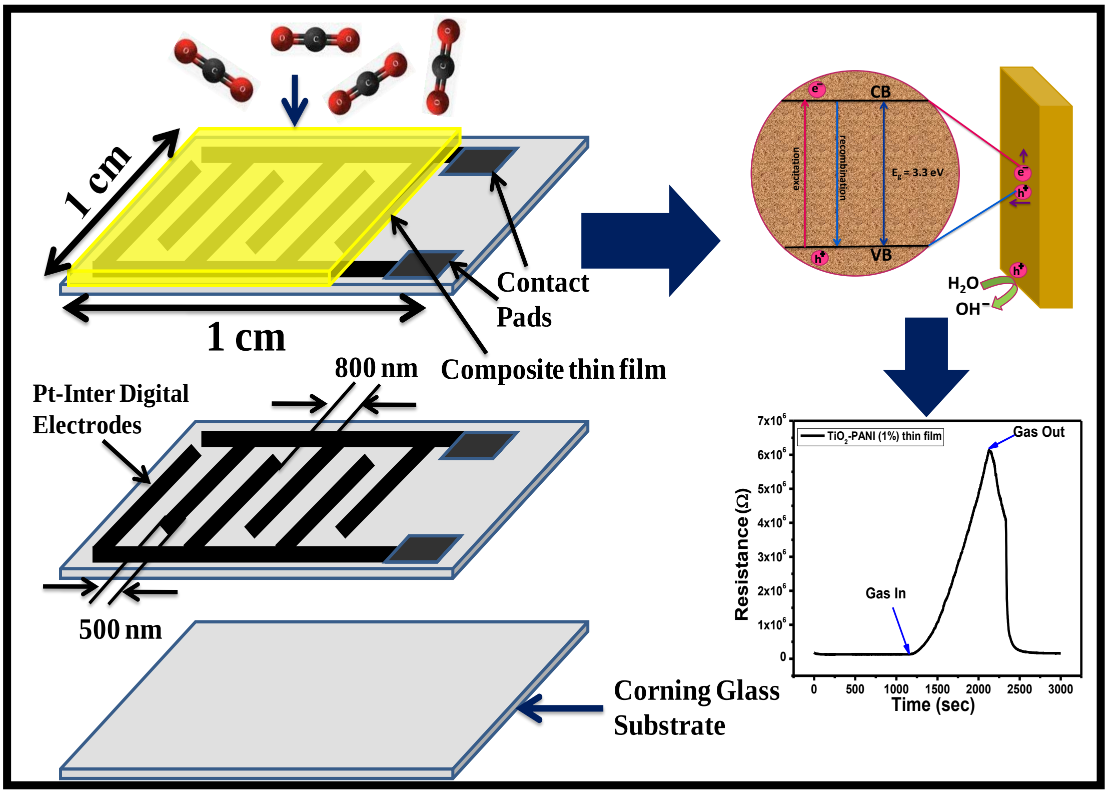

Figure 3 : Schematic of CO_2 sensing through PANI doped titanium dioxide composite thin film on corning substrate with IDEs

Chapter 4 describes the performance of a room temperature liquefied petroleum gas (LPG) sensor based on the Zn-doped titanium dioxide heterojunctions thin film prepared by spin coating technique. The surface morphology and structure of synthesised material were characterised by SEM and XRD analysis respectively. The structural analysis confirmed the formation of Zn-doped TiO_2 having an average crystallite size 76 nm with tetragonal rutile structure. Optical properties were investigated using UV–Vis absorption spectroscopy. Energy band gap of material was estimated as 3.26 eV. Variations in resistance with the exposure of LPG to the sensing element were observed. Sensor response (S) as a function of time was calculated and its maximum value was 2.92 towards 1.5 vol. % LPG, response time of the sensor was 120 s. The sensitivity of the

LPG sensor at 1.5 vol. % was found as 0.4625. Variations of average sensitivity of Zn-doped TiO_2 thin film with different volume concentrations of LPG is shown in Figure 4. The sensor was found moderately sensitive to LPG and results were found reproducible.

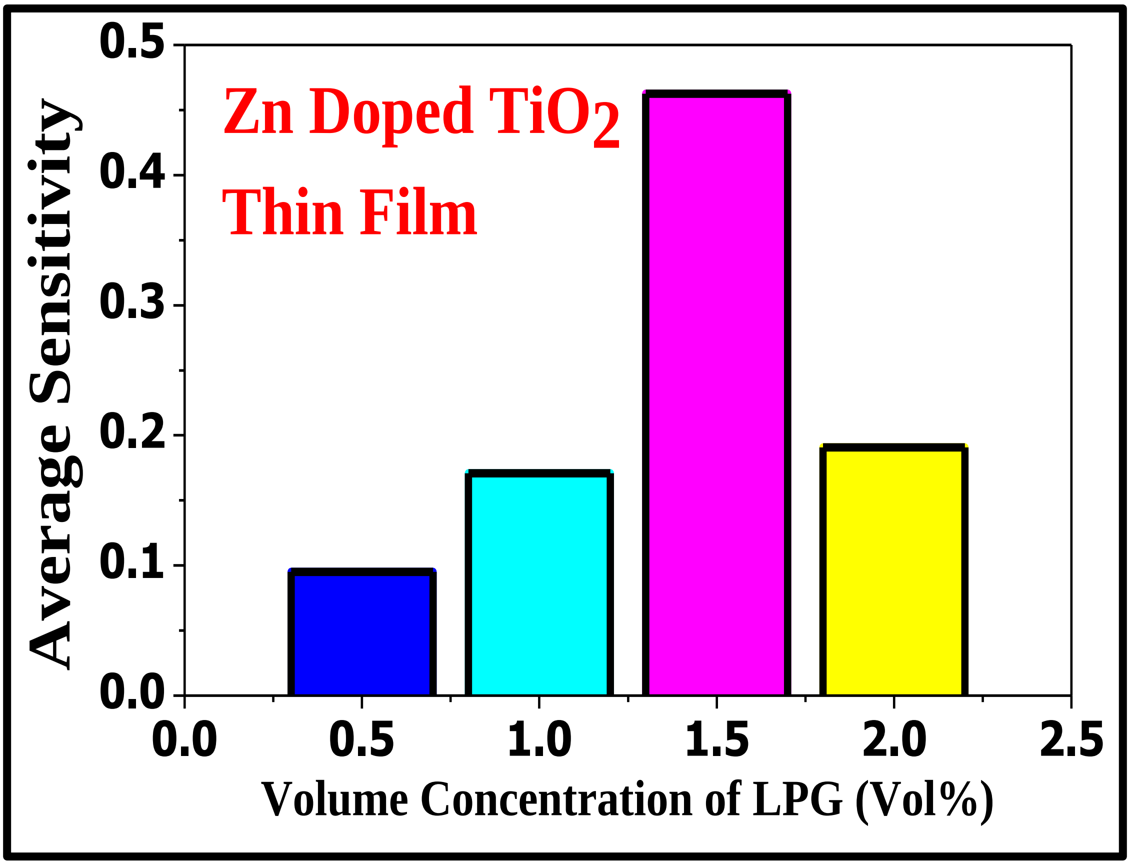

Figure 4: Variations of average sensitivity of Zn-doped TiO_2 thin film with different volume concentrations of LPG.

Chapter 5 includes the synthesis of Ag-doped TiO_2 nanocomposite via sol-gel method, its characterization and performance as liquefied petroleum gas (LPG) sensor. The synthesised material was characterised using XRD and confirmed the formation of (Ag-TiO_2) nanocomposite. The minimum crystallite size was found as 81 nm. XRD pattern revealed the tetragonal crystalline nature of the material. The material was also investigated through SEM and UV-Vis spectrophotometer. The energy band gap TiO_2 and Ag doped TiO_2 is found 3.29 eV and 2.6 eV by Tauc plot. The thin film was fabricated for the sensing analysis. Further at room temperature, the film was exposed to LPG in a gas chamber under controlled conditions at room temperature and variations in resistance with the concentrations of LPG were observed. Figure 5 shows the schematic diagram of working mechanism of LPG sensor for 0.1M Ag doped TiO_2 thin film. The maximum value of sensor response for Ag-TiO_2 thin film based sensor was found 3.82 for 2 vol.% of LPG. The response and recovery times were obtained as 13.2 s and 6.6 s respectively.

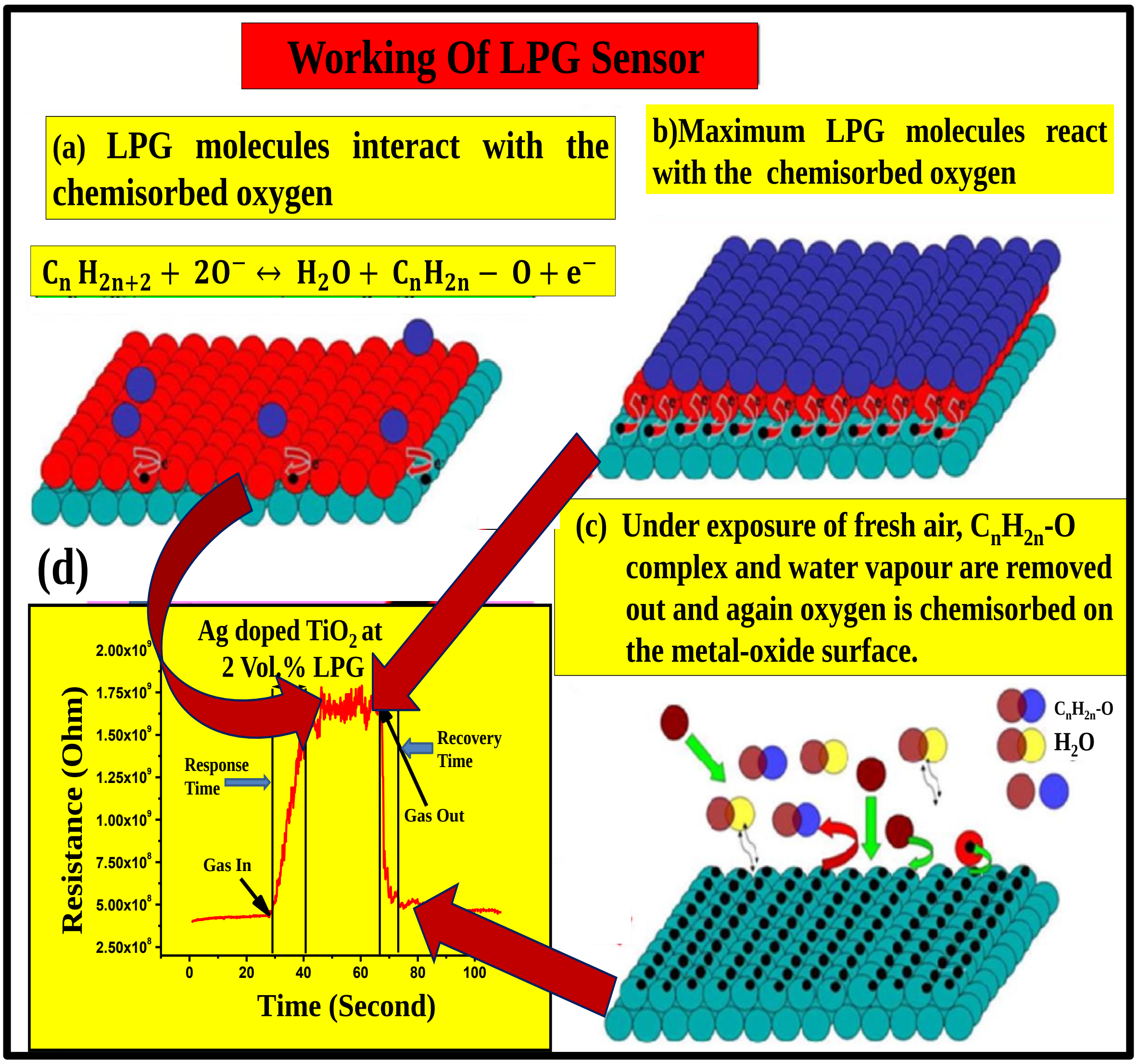

Figure 5: Schematic diagram showing the working of LPG sensor for 0.1M Ag doped TiO_2 thin film.

A chapter wise sketch of the thesis including the materials, percentage sensor response, crystallite size and concerned journals is depicted in Table 1. The main goal of our research work carried out was to design and fabricate a LPG sensor which would be robust, cost effective and more sensitive than previously reported sensors.

Table 1: A chapter wise sketch of the Thesis.

Chapters	**Sensing Materials**	**Target Gas**	**Concentration Of gas**	**Sensor Response**	**Response time(s)**	**Recovery time(s)**
Chapter 1	Introduction					
Chapter 2	TiO_2	LPG	4.0 vol. %	1.34	117	148
Chapter 3	PANI-TiO_2	LPG	2000 ppm	2.77	156	140
Chapter 4	Zn doped TiO_2	LPG	1.5 vol. %	2.92	120	102
Chapter 5	Ag-TiO_2	LPG	2.0 vol. %	3.82	13.2	6.6
Chapter 6	Concluding Remarks					

From Table 1, we deduce that the nanocrystalline Ag doped titanium oxide is an excellent material for LPG sensing application at room temperature and using this material a commercialized model of LPG sensor applicable for both indoor and outdoor detection of LPG may be designed. Thus various configurations/systems described in the thesis and the detailed specifications given for each of them are expected to prove useful in fabricating a sturdy, robust and cost-effective LPG sensor suitable for operation over the entire range; from lower explosive limit (LEL) to upper explosive limit (UEL).

Scope of Further Research

(i) In future, the effect of swift heavy ion irradiation and gamma irradiation on metal oxide semiconductor and related effect on their sensitivities and sensor responses as gas sensor with exposure of harmful gases in environment may be investigated.

(ii) Detailed analysis of the evolution of the surface reactions with respect to temperature in order to get precise understanding of the reaction products may be carried out.

(iii) An effort may also be made to integrate the reduced graphene oxide (rGO) doped nanostructured ZnO and SnO_2 by CVD or chemical route for LPG sensing application.

(iv) Theoretical modeling on sensing mechanism of LPG and other oxidizing gases with the metal oxides may be undertaken for further investigations.

(v) The presence of crystallographic defects affects the sensing mechanism of gas sensor. A quantitative study that associates the presence of these defects with the density of states in the energy gap followed by the variations in the sensitivity of the sensor is to be done.

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