Chapter

Design and Growth of Metal Oxide Film as Liquefied Petroleum Gas Sensors

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Abstract

Nowadays innovations in synthesis methods for metal oxide-based nanomaterials such as nanostructured and both physical and chemical route techniques have been adopted by various researchers around the world. The investigation has been focusing on various deposition parameters for fabricating nanostructured metal oxide. Gas sensors that use metal oxide materials are broadly utilized in industry to monitor combustion processes. While they are economical to powerful in high temperature environments, many of these instruments are not selective towards the species of interest when placed in a stream composed of multiple gases. Research on nanostructured metal oxide materials has generated great interest in scientific community. Metal oxide is a chemically stable, harmless, biocompatible, inexpensive material with very high dielectric constant and interesting photocatalytic activities. It is a wide-gap semiconductor and depending on its chemical composition, it shows a large range of electrical conductivity. Synthesis strategies regarding nanocomposites of metal oxide with other inorganic and organic materials sensing activities has been reviewed. The measure response of metal oxide film-based sensor highat low concentration of LPG.

Keywords: metal oxide, thin film, deposition technique, LPG sensor

1. Introduction

Liquefied petroleum gas (LPG) is the composition of hydrocarbons mainly propane and butane. The lower explosive limit (LEL) as specified by National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA) standards for chemical hazards is 21,000 ppm (2.1% by volume in air) for propane and 19,000 ppm (1.9% by volume in air) for butane. The permissible exposure limit (PEL) for LPG as specified by NIOSH and OSHA standards is 1000 ppm [1]. LPG is mostly used as fuel for vehicles and as cooking gas for household applications. Exact observing of leakages of LPG even at low concentrations can be useful to avoid accidental explosions [2, 3]. Sensors have turned into an indispensable piece of the cutting-edge human progress attributable to its significance, where metal oxides have played a major role as reliable sensor materials. Nanoparticle do research presents broad scope for the growth of novel solutions in the field of healthcare, cosmetics, optics and electronics. Varying their sub-atomic and nuclear states results in surprising results, which may not be conceivable by utilizing the materials in their unique states. A few metal oxides such as TiO_2, SnO_2, ZnO, WO_3 and Cr_2O_3, etc., are shown in semiconducting nature of materials. The electrical properties of these oxides are sensitive to the oxygen partial pressure since it changes in the concentration of electrons or electron holes in the oxides. This article manages the properties and utilizations of titanium oxide nanoparticles. Titanium oxide (TiO_2) is accessible as nanocrystals or nanodots having a high surface area.

Titanium oxide (TiO_2) nanoparticle is a non-broke down material which does not break up itself when degrades organic contaminant and kills germs. It has a lasting effect on killing germs and degrading organic contaminants. TiO_2 nanoparticle is broadly used as ultra violet-resistant nanomaterials and in the field of produce chemical fiber, plastics, printing ink, coating, self-cleaning glass, self-cleaning ceramic objects, antibacterial material, air purification, cosmetics, sunscreen cream, natural white moisture protection cream, moistening refresher, vanishing cream, skin protecting cream, foods packing material, coating for paper-making industry: used for civilizing the pliability and opacity of the paper and used for producing titanium, ferrotitanium alloy, carbide alloy, etc., in the metallurgical industry, astronautics industry, conducting material, gas sensor, and moisture sensor. TiO_2 also famous such as titania is the obviously occurring oxide of titanium. Titania is an inventive material used broadly in industry, research and environmental cleaning. Titania occurs in several crystalline forms; the most significant of which are anatase and rutile. Uncontaminated TiO_2 does not occur in nature but is derived from ilmenite or leucoxene ores. It is additionally eagerly mined in one of the most perfect structures, rutile shoreline sand. These minerals are the real crude materials utilized in the generation of titanium dioxide pigment. The initial step is to filter the mineral and is for the most part a refinement step. Either the sulfate process, which uses sulfuric acid as a removal agent or the chloride process, which uses chlorine, may achieve this. After filtration the powders may be treated to enhance their performance as pigments.

Therefore, metal oxide nanomaterials play imperative role in the recent development of science due to its small size and large surface area [4]. In this chapter several synthesis methods to prepare ceramic nanoparticles, characterization techniques and different properties of gas/humidity sensors are described. The role of water vapor has been studied in the environment with respect to human life. For the measurement of humidity, conventional approaches and modern methods using solid state devices are described. Nanomaterials can be metals, stoneware, polymeric materials, or composite materials. Their significant characteristic is a very small feature size in the range of 1–100 nm. At the nanomaterial level, some material properties are influenced by the laws of nuclear material science, instead of carrying on as conventional mass materials do.

1.1 Lattice structure of TiO_2

The three forms of titanium dioxide structure materials can exist: rutile, anatase and brookite shown in **Figure 1**.

The basic structural features of anatase and rutile materials have been assessed, as the brookite structure is not used regularly for exploratory examinations. Together, the crystal structures of rutile and anatase are found in the widespread octahedron. In rutile, the bending is slightly orthorhombic in which the unit cell extends beyond a cubic form. In anatase, the distortion of the cubic lattice is more significant and, therefore, the resulting symmetry is smaller than the orthorhombic one. **Figure 2** shows a structural drawing of rutile and anatase bulk materials. The lengths of the connections and the angles between the atoms are shown, showing the elongated cubic form [5].

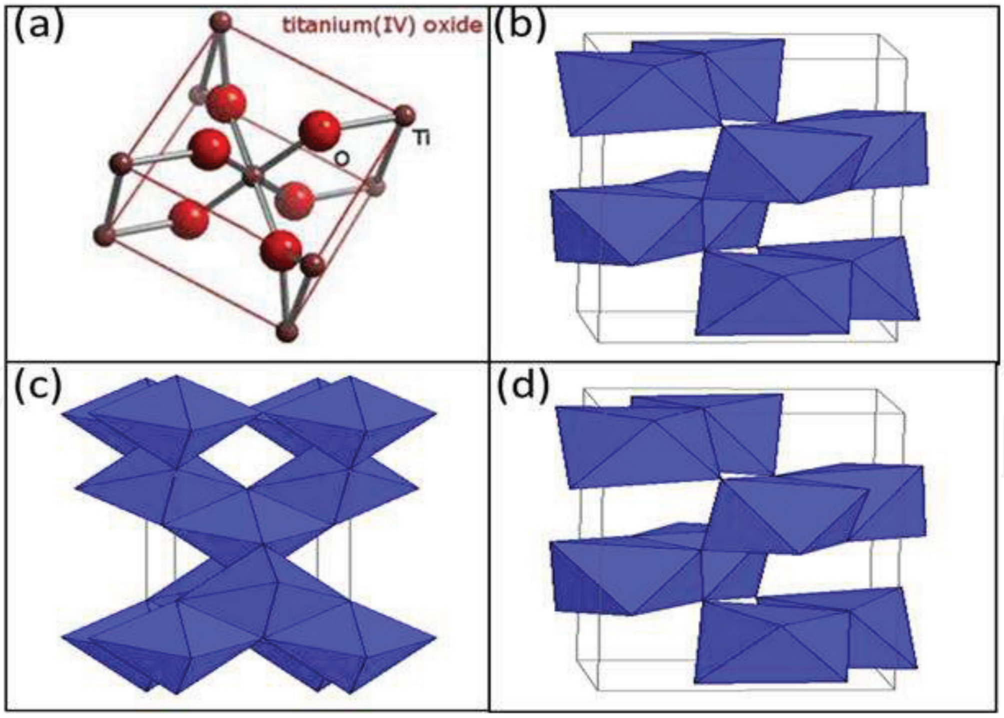

Figure 1.
(a) Unit cell of the crystalline structure of TiO_2 and crystal structure of (b) rutile (tetragonal) TiO_2, (c) anatase (tetragonal) TiO_2, and (d) brookite (orthorhombic) TiO_2.

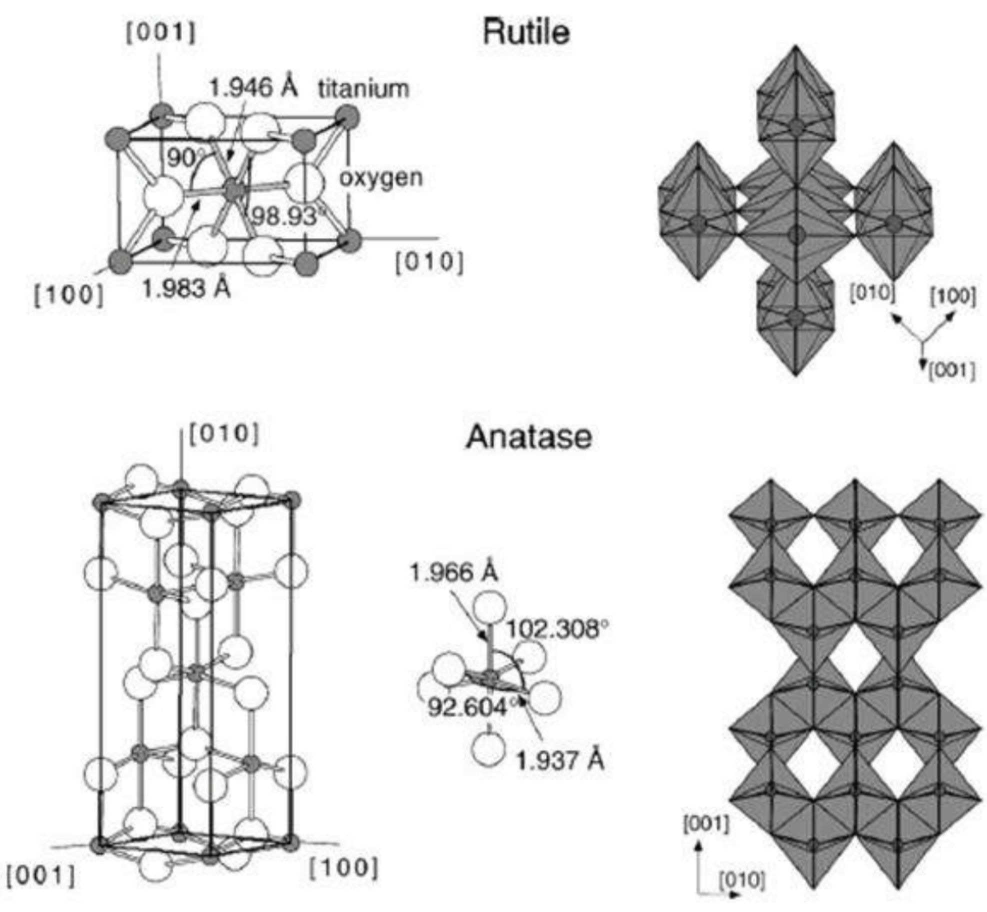

Figure 2.
The structure of rutile and anatase titanium dioxide.

The crystal structure of TiO_2 nanoparticles depend great extent on the arrangement technique. The tiny TiO_2 nanoparticle (<50 nm) anatase appeared to be steadier and more changed in to rutile phase at >973K. The change arrangement

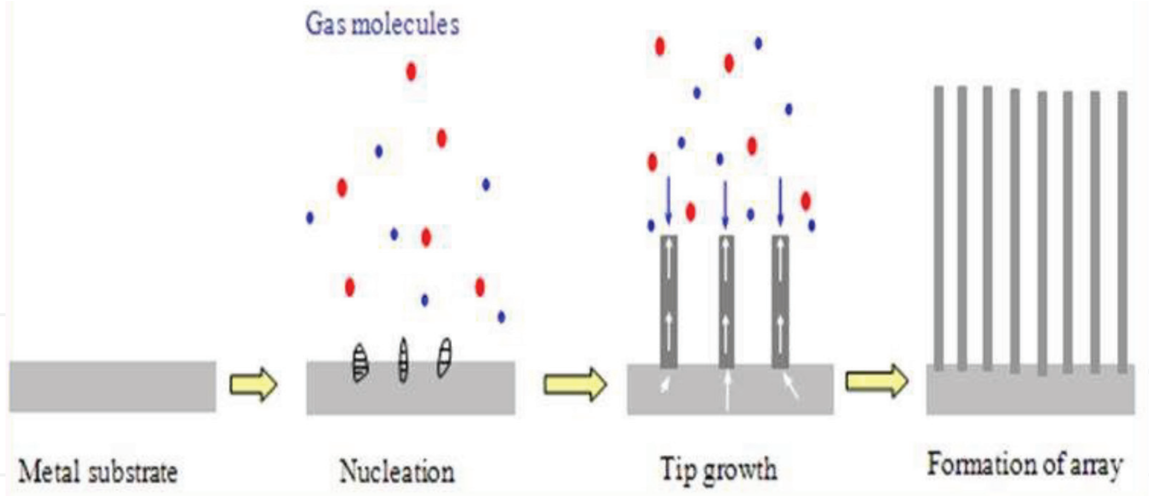

Figure 3.
The schematic diagram of growth of nanoparticles.

and thermodynamic stage steadiness relied upon the underlying molecule sizes of anatase appeared in **Figure 3**. In the temperature range 973–1073 K only one phase change from anatase to rutile occurred. Both sizes of anatase and rutile particles increased with increasing temperature, but the growth rate was different. Rutile had a much higher growth rate than anatase. The rate of development of the anatase has been stabilized at 800°C. The rutile particles, after nucleation, have grown rapidly, where the size of the anatase particles has remained virtually unchanged with the decrease of the initial particle size, the temperature of start the diminished transition [6]. The diminished warm steadiness in better nanoparticles was fundamentally because of the lessened enactment vitality as a size related surface enthalpy and stress vitality expanded.

1.2 Properties of TiO_2

The chemical composition of Ti and O in TiO_2 is as given in **Table 1**.

1.2.1 Key properties

The summarized **Table 2** shows the physical and mechanical properties of sintered titania, while the optical properties of titania are provided in **Table 3**.

1.2.2 Photo catalytic properties

Titania used a photosensitizer for photovoltaic cells and when used as an solid state coating electrode in photo-electrolysis cells, can improve the efficiency of electrolytic splitting of water into hydrogen and oxygen.

In 1972, Fujishima and Honda discovered the photocatalytic water division in TiO_2 electrodes. This incident developed the foundations of a new era inheterogeneity. photo-catalysis. Titania is a promising photocatalyst chemical. Two different crystal

Element	Content (%)
Titanium	59.93
Oxygen	40.55

Table 1.
Chemical composition.

Density	4 g cm^{-3}
Porosity	0%
Compressive strength	680 MPa
Poisson's ratio	0.27
Shear modulus	90 GPa
Modulus of elasticity	230 GPa
Resistivity (25°C)	10^{12} ohm cm
Resistivity (700°C)	2.5×10^4 ohm cm
Dielectric constant (1 MHz)	4
Thermal expansion (RT-1000°C)	9×10^{-6}
Melting point (°C)	1843°C
Boiling point (°C)	2972°C

Table 2.
Typical physical and mechanical properties of titania.

Phase	Refractive index	Density (g cm^{-3})	Crystal structure
Anatase	2.49	3.84	Tetragonal
Rutile	2.903	4.26	Tetragonal
Brookite		4.123	Orthorhombic

Table 3.
Titania optical properties.

structures of TiO_2, rutile and anatase, are normally used in photo-catalysis activity. Photo-catalysis is a photon energy (from the UV in sunlight) used to the medium (catalyst) to support chemical reaction to continue. TiO_2 is a semiconductor in which, the valence band is filled with electrons. Since the band gap of TiO_2 is 3.20 eV and can use only UV light below 400 nm, numerous efforts have been made to sensitize larger band gap semiconductors or to use slight band gap semiconductors that can absorb visible light. Photon or UV light which is below the wavelength of violet (400 nm) has a high destructive energy. When the photon is familiarized to titania, it becomes unstable thus the electron escapes. This electron can break chemical bond since it has a high energy. This reaction can be very useful to decompose organic material, impurities and bacteria in the air.

1.3 Synthesis methods of nanomaterials

Synthesis methods play very important part of research to control the size and surface area of nanomaterials. There is numerous synthesis methods, some of them are described below:

- Hydrothermal synthesis
- Sol-gel method
- Aerosol methods
- Low temperature combustion methods

1.3.1 Hydrothermal synthesis

The hydrothermal synthesis is a process which uses single heterogeneous phase reactions in aqueous medium at higher temperature and pressure to crystallize and produce ceramic materials hydrated directly from the solutions [7]. This synthesis offers a low temperature direct route to the oxide powder with a small size distribution that prevents the passage of calcination. The hydrothermal reaction mechanism monitors a liquid nucleation model. Normally, in the hydrothermal process temperature falls between the boiling point of the water and the critical temperature (T_c = 374°C), while the pressure is higher than 100 kPa. The product is washed with deionized water to remove ions from the solvent and other impurities. After drying in the air, very well dispersed ceramic nanoparticles are obtained.

1.3.2 Sol-gel method

First, a solution of the appropriate precursors (metal salts of organic metal compounds) is formed, followed by conversion into homogeneous oxide (gel) after hydrolysis and condensation [8]. The drying and subsequent calcination of the gel produce an oxide product. Usually, for the preparation of multicomponent oxides, the alkoxides are mixed in alcohol. The components for which alkoxides are not available are introduced as salts, such as acetates. The hydrolysis is carried out at a controlled temperature, pH and alkoxide concentration, addition of water and alcohol.

1.3.3 Aerosol method

This method is also defined as a gas phase method. It is considered to be convenient and convenient in the large-scale industrial production of multicomponent materials [9]. Aerosols are suspensions of small solid or liquid particles in a gas. There are two ways of preparing ultrafine particles by aerosol processes. The first concerns the generation of a supersaturated vapor from a reagent followed by a homogeneous nucleation (conversion of gas into particles). The second concerns the generation of liquid droplets, which are subjected to a heat treatment in solid particles (conversion of liquid into particles). The latter is used to prepare multicomponent materials.

Spray drying and spray pyrolysis are the most common methods for converting liquid into solid. A metal precursor (sol) solution is produced, followed by drop atomization, which are conducted to an oven. Therefore, spray drying can be a suitable process for consolidating the nanoparticles into submicronic spherical granules that can be compacted into microscopic shapes.

1.3.4 Low temperature combustion method

The low-temperature combustion synthesis technique (LCS, for its acronym in English) has proven to be an innovative, extremely easy path, which saves time and saves energy for the synthesis of ultrafine powders [10–13]. This is based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals and some organic fuels, which provides a voluminous and fluffy product with a large surface area. As starting materials, oxidizing metals salts, such as metal nitrates and a combination agent (fuel), such as citric acid, polycyclic acid or urea are used. Citrate acid is used more widely, since it does not function only as a reducing/fueling agent, but also as a chelating agent.

1.4 Introduction to gas sensor

1.4.1 Gas sensor technology

A gas sensor is a device that produces an electrical signal in response to a chemical interaction with the vapors because the information obtained from this process is advantageous. Gas sensors have generated extensive applications in both domestic and industrial environments. However, despite its value, there are many difficulties in making a reliable sensor before it can be used safely. Ideally, gas sensors should exhibit a high sensitivity to steam that are designed to detect. Furthermore, the sensor should produce only an electrical response when exposed to the gas of interest. The sensors must also have stable and reproducible electrical signals to reduce the time required for calibration. There are other practical concerns, such as minimizing size, weight and energy consumption, as well as the ability to position the sensor close to where measurements are to be made.

According to the definition of gas sensor, provided by the International Union of Pure and Applied Chemistry (IUPAC), "a chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific component of the sample to the analysis of the composition total, in an analytically useful signal. The above chemical information can derive from a chemical reaction of the analyte or from a physical property of the system under examination" [14]. Normally, chemical sensors consist of two main parts, a receiver and a transducer. A sensor is an instrument that responds to a physical stimulus (such as heat, light, sound, pressure, magnetism or movement). Collects and measures data related to some properties of a phenomenon, object or material. Sensors are an important part for any measurement and automation application. The sensor is responsible for converting a certain type of physical phenomenon into an amount that can be measured by a data acquisition system (DAQ). The receiver transforms the chemical information into a form of energy, which can be measured by the transducer. The transducer converts this energy into a useful analytical signal, typically electric. Chemical sensors are classified in different ways. One of the classifications uses the operating principle of the receiver [14].Using this principle, one can distinguish between.

1. Physical sensors,

2. Chemical sensors, and

3. Biochemical sensors.

In physical sensors a chemical reaction does not take place in the receiver and the signal is the result of a physical process, such as mass, absorbance, refractive index, temperature or conductivity change. Chemical sensors are based on chemical reactions between the analyte molecules and the receptor. Biochemical sensors are a subclass of chemical sensors, in which the reaction is biochemical. Typical examples of such sensors are microbial potentiometric sensors or immune sensors. It is not always possible to discriminate between physical and chemical sensors. A good example is a gas sensor, in which the signal is the result of gas adsorption.

Gas loss is a major concern in residential, commercial and gas transportation vehicles. One of the precautionary measures to avoid the danger associated with gas leaks is to install a gas leak detector in vulnerable locations. The purpose of this document is to present the design of an automatic economic alarm system, capable of detecting liquefied petroleum gas leaks in different locations. In particular, the designed alarm system has a high sensitivity, especially for butane, which is also sold individually bottled as fuel for cooking and camping. The proposed system is designed to meet UK occupational health and safety standards. Test results are proven for a USB powered gas leak detection system and provide early warning signals in less severe conditions and trigger an acute alarm in case of emergency to protect users. Liquefied petroleum gas (LPG) is commonly used in homes for central heating, hot water, gas ovens, kitchens and mobile heaters for recreational activities such as boats, caravans and grills. This energy source is mainly composed of propane and butane, which are highly flammable chemical compounds. LPG leaks can occur, though rarely, in a home, commercial facility, or gasoline vehicle. Loss of this gas can be dangerous as it increases the risk of fire or explosion. The victims of this danger are still common news in the media. Since LPG as such has no odor, gas/refinery companies add an odor, such as ethanediol, thiophene or mercaptan, so that most people can detect losses [15]. However, it is possible that some people with reduced sense of smell cannot rely on this intrinsic safety mechanism. In such cases, a gas leak detector becomes vital and helps protect people against the dangers of gas leaks. Several research papers on gas leak detection techniques have been published [16–24]. In [16] a home wireless security gas leakage system [16] was proposed in which the alarm device provides mobility within the house's premises. Detection of losses and identification of their position is the most important task of pipeline operators in the gas industry. Flow monitoring and methods based on linear parameter variation models (LPV) are widely used in the gas industry to detect gas leaks. Both methods continuously measure pressure at different sections of the tube, usually at the ends [17–22]. However, the disadvantage of these techniques is that they rely heavily on the noise of pressure/temperature measurements. The reliability problems of gas leak detectors were addressed in [23]. The gas leak sounds generated by the cracks in the tubes were analyzed in [24] to locate the leak.

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 science of nanomaterials deals with new phenomena and new sensor devices that exploit these phenomena are being built. Sensitivity may increase due to better conduction properties, detection limits may be lower and very small amounts of samples may be analyzed, direct detection is possible without the use of labels and some reagents may be removed [25].

Inorganic nanomaterials with controllable sizes and shapes have a wide range of unique physical, chemical, electrical, surface and optical properties. Nanometric sensors are essential for many interesting developments in nanotechnology research. Several "bottom-up" techniques widely reported in parallel offer the potential for the integration of high-density nanosensors beyond the capacity of conventional technologies with a small fraction of the current manufacturing cost. The field of nanosensors requires the identification of several self-organized nanostructures with structural characteristics and special physical properties to have devices with the appropriate integration of the circuit [26].

The large surface-to-volume ratio of nanomaterials can be used as an advantage for the development of the gas sensor. The large surface to volume ratio of nanocrystalline structures increases the opportunity for this surface reaction. This in turn will increase the sensitivity of the gas sensor. Engineering materials with selective chemistry to modify and manipulate the structure is the key to the improvement in gas sensor sensitivity and selectivity. Nanomaterials have been highlighted for gas sensor applications due to their enhanced abilities over their conventional entering material counterparts. The surface of nanomaterials can comprise much of the actual material making them ideal for gas sensors. Ability to synthesize one dimensional nanostructure with extremely high aspect ratios makes them attractive in gas sensor fabrication as well. The space charge layer control of nanostructures makes them particularly interesting since conduction can change drastically with expansion and contraction of the layer in the presence of different gases. Despite these observations at the nano-scale, many of the mechanisms responsible for conduction at the nano-scale are still poorly understood. The oxygen vacancies also need to not be "pinned" to any impurities and need as little resistance as possible at the grain boundaries when the appropriate reducing gas is present. Second, increasing the number of surface sites for gas interaction will help achieve this goal; so that even low concentrations of gas can be detected at room temperature. The use of nanomaterials is important because of their high surface/volume ratio. This can be increased by changing the nanoparticle shape from spherical to unidimensional, creating hollow tubes or tubes. The third modification that can be made to the sensor material is the modification of the space-loading layer. This is done to obtain the maximum signal change in the presence of the target gas. Modification of the space charge layer can be done by: (1) reducing the size of the crystallite, (2) changing the chemistry of the defects within the space charge layer and the surface of the material, and (3) changes in the charge layer space. The shape of the particle may play a factor. Another interesting aspect of nanomaterials that make them a candidate for room temperature gas sensor applications is the fact that changes in the band gap have been reported at extremely small sizes. The possibility to modify this band gap may be another way to improve room temperature gas sensing by changing the potential barrier energy required for charged species to conduct. Another enhanced feature of nanocrystallites is their conduction of electrons from the surface reaction. These conduction electrons have to overcome a potential barrier induced by the space charge layer. The magnitude of this space charge layer is dependent on the crystallite size (D) as well as the space-charge layer thickness (L). It has been shown that when $D < 2$ L, the sensitivity of a gas sensor is enhanced drastically. This $D < 2$ L limit can be reached when employing nanostructures.

1.4.2 Importance of a gas sensor

Gas sensors are very important in the industrial sector and in other areas. Although there are many difficulties in solving these problems, gas sensors still have several specific functions in theworld. For example, hydrogen sensors are needed in the rocket propulsion industry because the dispersion of the hydrogenpropellant presents significant safety risks. In addition, theautomotive industry routinely monitors the air/fuel ratio invehicles with oxygen sensors that use an electrochemical cell containing TiO_2 that conducts oxygen ions at high temperatures. The automotive industry is also interested in NOx sensors because nitrogen oxides are formed when the fuel is burned at high temperatures. Nitrogen oxides are a unique hazard because they can travel long distances from their emission source and generate ozone, pollution and particles away from the actual source of contamination. Carbon dioxide sensors are an example of devices that have found multiple uses; they are required for indoor air quality operations and for food storage and processing incubators. In addition, hydrocarbon sensors are required to monitor aeronautical and automotive discharges, leak detection and fire detection. Hydrocarbons are also a precursor of tropospheric ozone, and it is known that some types of hydrocarbons are toxic. Clearly, there are many requirements for accurate and reliable sensors in the environment:

- The material should sensitive in lower explosive limit (LEL) for explosive gases.
- The material should have high sensitivity over a wide range of humidity and temperature.
- It should quickly respond to any fast changes in the ambient.
- The sensor material should have rapid response to the variation of gas concentration and good reproducibility of the electrical signal.
- The sensitivity should be independent of the ambient temperature.
- The material should not react with any chemical contaminants present in the application ambient.
- It should show stable characteristics for a long time.
- It should be less portable.
- The construction of the sensor should preferably be simple using IC technology and of low cost.
- The device should be operated by a battery.

1.4.3 Gas sensing method

1.4.3.1 Properties of LPG

The LPG gas consists of isobutene, propane, methane, etc. In 1910, LPG [27], first produced by Dr. Walter Snelling of the United States Department of Mines, studied gasoline to understand why it evaporated so quickly and found that the gases that evaporated were propane, butane and other light hydrocarbons. Both LPG and natural gas respect the environment and are easily detectable. These gases are usually stored in pressurized steel cylinders in liquid form and vaporized at normal temperatures. By comparing air with LPG, it is heavier that it flows through the ground and even installs at low points that make it difficult to disperse. LPG is a blend of commercial butane and commercial propane with saturated and unsaturated hydrocarbons. Due to the versatile nature of LPG, it is used for many requirements such as domestic fuel, industrial fuel, automotive fuel, heating, lighting, etc. And the demand for LPG increases exponentially every day. Gas leaks caused by fatal hell have become a serious problem in homes and other areas where domestic gas is handled and used. Gas leaks cause several accidents that result in financial losses, as well as human injuries and/or losses. The LP gas property is shown in **Table 4**. The explosion occurs when the following three conditions are satisfied:

Gas	Formula	%LEL	%UEL	Ignition temperature	Flash point in (°C)
Propane	C_3H_8	2.2	9.5	470	97
Butane	C_4H_{10}	1.8	8.4	365	152

Table 4.
Properties of LPG.

- The concentration of gas is between LEL.
- A sufficient amount of oxygen exists.
- There is a source of ignition [28].

1.4.3.2 Liquid petroleum gas sensor

Coal gas and liquefied petroleum gas (LPG) are combustible gases. They are potentially dangerous because explosions may occur when accidental or accidental spills occur. Therefore, detecting it in household appliances is very important for safety. One of the most common types of domestic energy source is propane, which contains liquefied gas. Although safety issues are considered by the company, gas leaks have become a very common incident that can cause damage to human lives and property. The system has two main devices: the gas detector and the centralized alarm unit. Alarms are missing during cooking, which requires the equipment to detect LPG.

There may be more than one detector in the systems, which can be identified separately in the system. The centralized alarm unit detects alarms sent by the detectors and releases the alarm. It has an indication of which detector has released the notice. The alarm unit has AC power and has a battery backup to solve power problems. The components of the device were chosen taking into account the energy consumption and the time intervals were calculated in relation to the current consumption of each component. Liquefied petroleum gas is a flammable mixture of hydrocarbon gas used as fuel in heating appliances and vehicles. The varieties of LPG bought and sold include mixtures that are mainly propane (C_3H_8), mainly butane (C_4H_{10}) and, more commonly, include propane and butane, depending on the application [29].

Unlike natural gas, LPG is heavier than air, unlike natural gas, so it will flow through floors and will tend to settle in lower locations such as basements. There are two main dangers of this [29].

1. Possible explosion if mixture of LPG & air is right & if there is an ignition source.
2. Suffocation due to LPG displacing air, causing a decrease in oxygen concentration.

1.4.3.3 Basic principle of solid state gas sensors

The basic principle of solid state gas sensors is schematically illustrated in **Figure 4**. Solid state gas sensors are based on adsorption/desorption or chemical reactions of target gases on the surface or grain boundaries of sensing material and lead to physical changes like in temperature, mass, conductivity, refractive index, etc.

Although the basic principle behind solid state sensors seem to be similar, multitude of sensor technologies have been developed. Conducting polymers are under the category of resistive sensors and its conductance changes with the interaction of sensing gas molecules. Although polymer sensors are operated at room temperature but drift in their response with time and sensitivity to ambient conditions are of major concern. The semiconductor metal oxide gas sensors are in the form of thin ceramics or films and operate at high temperatures. The resistance of these sensors changes in the presence of sensitive gas (oxidant or reducer). However, the energy consumption of these sensors is high and could be reduced to some extent by using MEM-based structures. The surface plasmon resonance (SPR) technique was also used for gas detection, based on the principle that when a target gas interacts with a

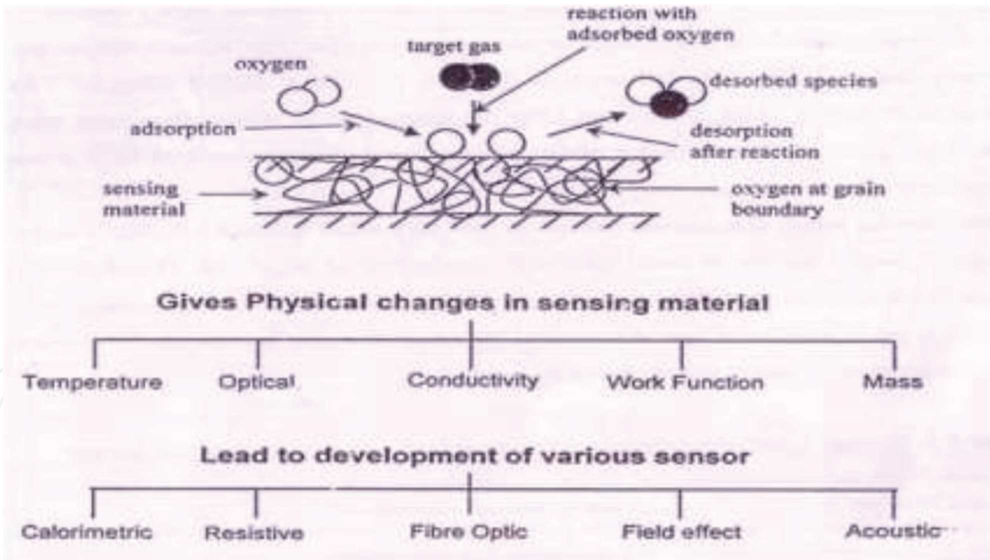

Figure 4.
General principle of solid state gas sensors.

Physical changes	Type of sensor devices
Conductivity	Semiconducting metal oxide conducting polymer.
Optical	Fibre optic, thin film: SPR, reflection interferometry, adsorption, fluorescence.
Work function	Field effect device: diode, capacitor, transistor, Kelvin probe.
Heat generation	Pt-wire, thermopile, thin film resistor.
Dielectric permittivity	Capacitor.
Mass	Quartz crystal microbalance. Surface acoustic wave.

Table 5.
Various types of solid state sensors and the respective physical changes.

metal film, the optical property (refractive index) changes. The change of the refractive index before and after the interaction of the chemical species with a metal layer gives the concentration of the target gas. The main disadvantage of SPR is complicated optics and the system is not easy to use. The problem of selectivity is another critical problem. The gas sensors based on the field effect transistors depend on the change in the working function of the metal gate with the interaction of the target gas. However, the design is complicated, and the characteristics are very sensitive to environmental conditions. **Table 5** lists several types of solid-state gas sensors and the respective expected physical variations due to the interaction of the target gas.

1.5 Sensor parameters

It is very much important to understand the sensing parameters of a good sensor. These are defined as:

- Sensing response,
- Operating temperature,
- Response time and
- Recovery time

There are some of the salient parameters that are associated with measurement of response characteristics of a gas sensor.

c. Sensing response:

The response (S) of a gas sensor to a target gas at a given temperature T is determined from the measured value of resistance of the sensing element (SnO_2 thin film) in the absence (Ra) and presence of the sensing gas (R_g). The sensor response S is defined as:

$$S = \frac{R_g - R_a}{R_a} \quad (1)$$

where $R_g > > R_a$ for oxidizing gases, and therefore to a good approximation

$$S \approx \frac{R_g}{R_a} \quad (2)$$

a. Response time (T_{res}):

The response time is defined as the time taken by the sensor to acquire 90% of its maximum resistance value in the presence of target oxidizing gas.

b. Recovery time (T_{rec}):

The recovery time is defined as time taken by the sensor to reacquire about 10% higher value of its initial resistance in the presence of atmospheric air.

The typical variation in the response (S) of a gas sensor with temperature for a specific concentration of target gas is shown in **Figure 5**. A maximum in the response (S_{max}) at a certain critical temperature (T_{opt}) is referred to as the operating temperature of the sensor.

Response (t_{res}) and recovery (t_{rec}) time characterization of a typical sensor are shown in **Figure 6** which gives a clear picture about the increase in resistance value as soon as any oxidizing gas comes in contact with n-type semiconducting sensing layer. The sample regains its original resistance value (R_a) as soon as the sensing gas is expelled out from its vicinity.

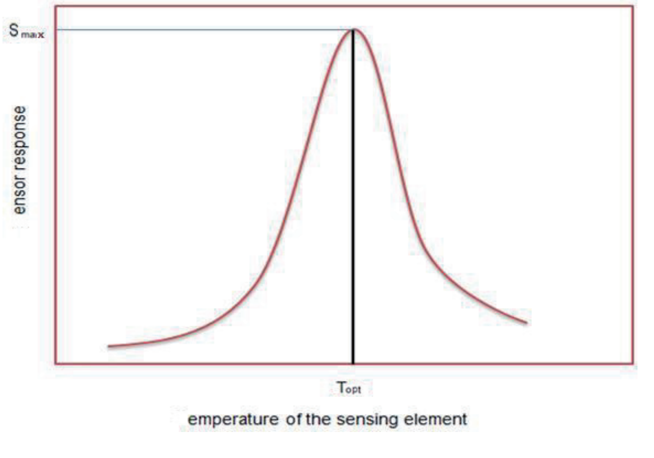

Figure 5.
Variation of sensor response with temperature for a typical sensor.

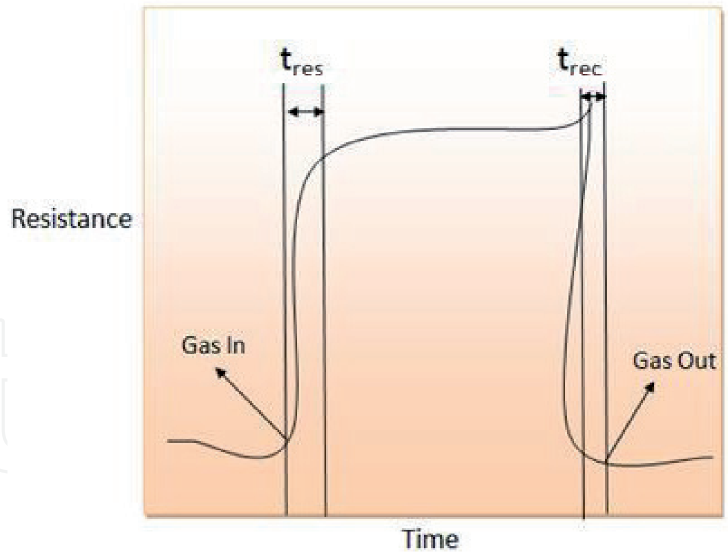

Figure 6.
Sensor response as a function of time, defining response time and recovery time of a typical sensor in response to an oxidizing gas.

The gas sensing mechanism of LPG sensor is a surface-controlled phenomenon, i.e., it is based on the surface area of the thin film. Initially, oxygen from the atmosphere gets adsorbed on the surface of the film and pick up electrons from its conduction band. In the present investigation, an exertion has been built up LPG detection with metal oxide (TiO_2) thin film arranged by the chemical route method which recognizes a leakage of LPG at operable RT. The surface mechanism of thin film-based sensor is governed by surface reaction. The change in resistance of thin film sensor in the presence of LPG molecule is prescribed by the oxygen species on the surface. However, the LPG sensing reaction mechanism is given [30]. The oxygen atoms were adsorbed the surface of metal oxide thin film when subjected to air. Various ionic species such as O_2, O_2^-, O^- or O^{2-} available on the surface of film plays a important task in the detection of gases. Oxygen captures the electron from the conduction band of metal film and is adsorbed on the surface as O^- ions, which are given as below:

$$O_2(gas) \leftrightarrow O_2(ads) \text{ (Thin Film Surface)} \quad (3)$$

$$O2(gas) + e^- \leftrightarrow O_2^- \text{ (Thin Film Surface)} \quad (4)$$

The adsorption of O_2^- ions on the nanostructured TiO_2 surface is vital to enhance the receptor function of the sensor, and, hence, its sensing response. The stabilization of surface resistance (R_a) results into the equilibrium of chemisorption process (state of saturation). **Figure 7** shows the sensor stabilization characteristic of metal oxide through different steps: (a) the conduction electrons are thermally excited in thin film (b) the electron donation by thin film to the oxygen, (c) physisorbed of oxygen atoms on the surface of metal oxide. The curve (d) of **Figure 7** shows the stabilization value of sensor resistance with time. When metal oxide film was exposed to LPG, it responds with the chemisorbed oxygen and a surface charge layer would be framed. The electron transfer from the conduction band to the chemisorbed oxygen results in the decrease in electron concentration at the film surface. As a consequence, an increase in the resistance of the film was observed before exposure to LPG. When the LPG reacts with the surface oxygen ions then the combustion products such as water depart and a potential barrier to charge transport would be developed, i.e., this mechanism involves the displacement of

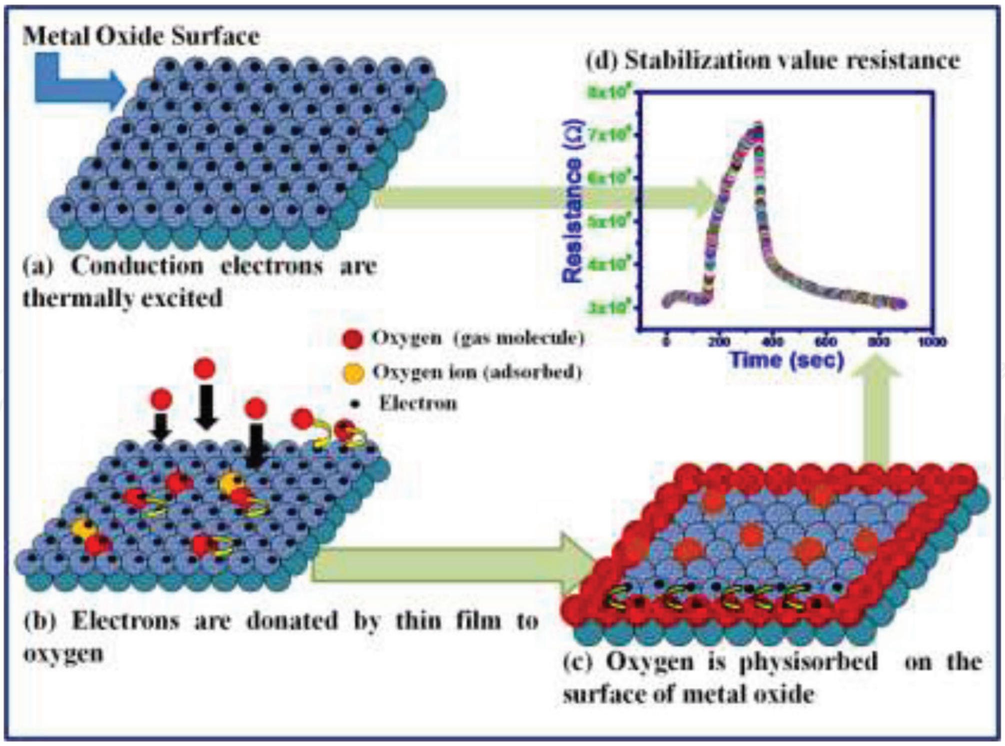

Figure 7.
Proposed model of sensing stabilization of metal oxide thin film.

adsorbed oxygen species by formation of water. The overall reaction of LPG with the chemisorbed oxygen may takes place as shown below [31]:

$$C_nH_{2n+2} + O_2^- \rightarrow C_nH_{2n}O + H_2O + e^- \quad (5)$$

where, C_nH_{2n+2} represent the various hydrocarbons. Due to the release of electrons, the resistance of the sensitive film decreases dramatically at first due to rapid absorption, after which it slowly decreases and eventually becomes saturated. When the flow of LPG stops for the study of the recovery characteristics, the oxygen molecules in the air will be absorbed on the surface of the film and the capture of electrons through the process indicated in the equations will increase the resistance of the sensor. Because the detection mechanism is based on the reaction of the chemisorption that occur on the surface of the film, the increase in the specific area of the sensitive material leads to multiple sites for the adsorption of the target gas. The function of the receiver is a capacity of the sensitive surface to receive the target gas that is directly related to the surface capacity of the adsorbed O_-^2 ions. In the present sensor at room temperature when the complex $C_nH_{2n+2} - O + H_2O$ produced throughout Eq. (5), the delivered water vapor being lighter than gas stimulated to the highest point of chamber was released out from the chamber by rotary vacuum, greater the capacity of the surface to receive the target gas, the greater the change in the resistance of the sensor and, therefore, the improvement of the sensory response of the sensor.

1.6 Requirements of a gas sensor

LPG is a combustible gas and it is widely used as a fuel for domestic heating and industrial use. Although it is one of the extensively used gases, it is hazardous. Hence, it is crucial to detect it in its early stages of the leakage and to perform the active suppression. For designing a robust gas sensor, the sensor material should possess following qualities given as under:

- The material should sensitive in lower explosive limit (LEL) for explosive gases.
- The material should have high sensitivity over a wide range of humidity and temperature.
- It should quickly respond to any fast changes in the ambient.
- The sensor material should have rapid response to the variation of gas concentration and good reproducibility of the electrical signal.
- The sensitivity should be independent of the ambient temperature.
- The material should not react with any chemical contaminants present in the application ambient.
- It should show stable characteristics for a long time.
- It should be less portable.
- The construction of the sensor should preferably be simple using IC technology and of low cost.
- The device should be operated by a battery.

2. Conclusions

Nanostructured semiconducting materials are the most promising materials for study of sensors because of their much surface to volume ratio. We have been interested in carrying out our investigations with a new material that possess good sensitivity for the LPG concentration at the LEL level, with properties that are stable over time and thermal cycling after exposure to the various species likely to be present in the ambient. Titania show very good surface reactivity and they have temperature dependent surface morphology. In this chapter, thorough experimental investigation was carried out in order to develop electrical type LPG sensor using thin films of nanosized Titania with some other additives material.

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Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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