BORANG PENGESAHAN STATUS TESIS

JUDUL: ROOM TEMPERATURE OF LIQUEFIED PETROLEUM GAS (LPG) SENSOR BASED ON p-La_2O_3/n-Fe_2O_3

SESI PENGAJIAN: **2007/2008**

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ROOM TEMPERATURE OF LIQUIFIED PETROLEUM GAS (LPG) SENSOR BASED ON p-La_2O_3/n-Fe_2O_3

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A thesis submitted in fulfillment of the
requirement for the award of the degree of
Bachelor of Chemical Engineering
(Gas Technology)

Faculty of Chemical and Natural Resources Engineering
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MAY 2008

I declare that this thesis entitled 'Room Temperature Liquefied Petroleum Gas Sensor Based on p-La_2O_3/n-Fe_2O_3' is the results of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted candidature of any degree.

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Special dedicated to my beloved mother and father

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ABSTRACT

Recently, owing to environment and safety aspect, interest in utilization of gas sensor is increasing. Gas sensor is used to detect hazardous gas in order to avoid it from spread to the environment. Lanthanum oxide and iron (III) oxide was chosen because of their availability and cost effective. Performance of using lanthanum oxide and iron (III) oxide as sensing element were investigated. Detection of liquefied petroleum gas in this research reported has a very long response time due to the chemical properties of lanthanum oxide. The p-La_2O_3/n-Fe_2O_3 sensor has detected the LPG 20 minutes after start flowing the gas inside the modified plastic bottle. This paper also describe the study on thermal stability of each substrate has been done using Thermogravimetric Analysis (TGA). Thermogravimetric Analysis is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. Lanthanum oxide shows that at 800^0C their original form will be transform into another phase of oxide such as LaO and LaO_2. Iron (III) oxide still remains their original form to the end of the sintered.

ABSTRAK

Dewasa ini, disebabkan oleh factor alam sekitar dan juga aspek keselamatan, kehendak terhadap penggunaan pengesan gas kian meningkat. Pengesan gas digunakan untuk mengesan gas-gas yang berbahaya daripada terbebas ke persekitaran. Prestasi penggunaan lanthanum oksida dan ferum (III) oksida sebagai alat pengesan dikaji. Lanthanum oksida dan ferum oksida dipilih disebabkab oleh mudah di dapati dan juda harganya yang efektif. Pengesanan liquefied petroleum gas di dalam kajian ini dilaporkan mengambil masa yang agak panjang disebabkan oleh sifat kimian lanthanum oksida. Alat pengesan p-La2O3/n-Fe2O3 telah mengesan LPG selama 20 minit selepas gas itu dialirkan ke dalam bekas plastik. Selain itu, di dalam laporan ini juga menerangkan kajian terhadap kestabilan therma setiap bahan menggunakan thermogravimetric analisis (TGA). Thermogravimetric analisis ini adalah sejenis ujian terhadap prestasi sampel untuk melihat perubahan di dalam berat disebabkan oleh perubahan suhu. Kajian ini menunjukkan ketelitian terhadap tiga parameter iaitu berat, suhu dan perubahan suhu. Lanthanum oksida menunjukkan pada suhu 8000C struktur asalnya akan berubah kepada fasa oksida yang berlainan seperti LaO atau LaO2. Manakala ferum (III) oksida pula kekal pada fasa asalnya sehingga tamat proses pembakaran.

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Nowadays the semiconductor gas sensors are broadly applied to the atmosphere monitoring system, the toxic or explosive gases detection system, the chemical processing facilities, the intelligent buildings with environmental control functions and so on. Gas-sensing materials can be classified mainly into two kinds: organic and inorganic materials. Doped or undoped SnO_2 is the most studied and used among the inorganic materials, but its operation temperature is about 150^0C-350^0C. It is actually have nine types of gas sensor or in other word there are nine technologies in gas sensor which is semiconductor – resistive, semiconductor – voltage, amperometric, catalytic, infrared, photo-ionization, fluorescent, surface acoustic wave and vibrating beam and capacitive. Every technology that stated above has their advantages and disadvantages. From all this technology, semiconductor is commonly used because of their better efficiency and low cost. Gas sensor main application is to detect hazardous gases that can harm people when it is spread to atmosphere. So using gas sensor will be detected a leaking of hazardous gas to the atmosphere.

1.2 Problem statement

Commercial solid state gas sensors based on semiconducting metal oxide, use property that gas changing the surface charge carrier concentration of semiconductor to cause changes in its electrical conductivity. This mechanism of the detection will help to monitor hazardous gases and to detect the threshold level of gases present in the atmosphere. However, these sensors showed poor performance with respect to the sensitivity at low concentrations of gases, selectivity and long-term stability. Metal oxide also will only detect at temperature range 150^0C to 350^0C. The gas-sensing devices based on organic materials, such as polypyrrol, polyaniline, and metaphthalocyanines, have gas sensitivity at room temperature, but their long response time (min) due to the orderly structure limits their usage. Consequently, there is a need for development of cost effective sensors to monitor LPG at room temperature.

1.3 Objective

In current research, the objectives are:

1. To characterize fabricated semiconductor/metal oxide.
2. To detect LPG in a room temperature.

1.4 Scope of study

Based on literature review, the scope of study for this research are:

1. To design simple experimental sensor for detection of LPG.
2. To study the LPG sensing properties in a room temperature.
3. To study thermal stability of La_20_3 and Fe_2O_3 using thermo gravimetric analysis.

1.5 Current Research

My research is to develop a cost effective sensors to monitor LPG at room temperature. This proposal used to describe a technique to form an n-Fe_2O_3/p-La_2O_3 hetero-junction. These characteristics in part are a requirement for further use of the devices in a variety of sensor applications. The n-Fe_2O_3/p-La_2O_3 hetero-junction in pellet form has been fabricated using hydraulic press.

This research will use semiconductor resistive method. This gas sensor will used n-Fe_2O_3/p-La_2O_3 junction as their sensing element. Lanthanum oxide has largest band gap of the rare earth oxides at 4.3 eV, while also having the lowest lattice energy, with very high dielectric constant, ε = 27 pF/m. Lanthanum oxide has p-type semi-conducting properties because its resistivity decreases with an increase in temperature, average room temperature resistivity is 10^3 Ω cm.

CHAPTER 2

LITERATURE REVIEW

2.1 Type of Gas Sensor

Nowadays there are variety of gas sensor that been develop for many reasons. Each gas sensor has their advantages and disadvantages. So research has been made to maximize their ability and reduce their disadvantages. The existing gas sensor in market is like:

(a) Hydrogen Gas Sensor
(b) Carbon Dioxide Gas Sensor
(c) Butane Gas Sensor
(d) Propane and Butane Semiconductor Gas Sensor
(e) Liquefied Petroleum Gas Sensor

2.1.1 Hydrogen Gas Sensor

A fuel cell with hydrogen energy is recently expected as a new energy source. However, because hydrogen concentration over 4% has the risk for an ignition, the development of sensors for quickly detecting the leakage of hydrogen has been advanced. At present, various types of sensors have been studied, such as Schottky diode type, field effect transistor (FET) type, etc. The characteristics of these sensors strongly depend on those of catalytic metals, because the principle of them is based on the work function change of catalytic metals. Therefore, it is essential to clarify the hydrogen adsorption mechanism on catalytic metals. FET type sensors using catalytic metals have been developed since 1975. These sensors have a number of advantages, which are room temperature operation, smaller size compared to the conventional sensors and low power consumption. Recently, we reported the fast response mechanism of the FET with platinum gate electrode (Pt–FET) to hydrogen in nitrogen. However, the detection of hydrogen in air is generally required for practical applications, therefore, it is necessary to investigate the hydrogen response mechanism to hydrogen in air in detail. This paper reports the effect of oxygen gas in air on the Pt–FET. (Yamaguchi T, 2006)

2.1.2 Carbon Dioxide Gas Sensor

The increasing number of vehicles using our roads annually has led to rising levels of pollution entering our atmosphere. The exhaust pollutants are a mixture of noxious gases and particulates. The gases include carbon monoxide, hydrocarbons oxides of nitrogen and oxides of sulphur. These pollutants are produced under different engine combustion conditions. CO is produced when fuel is not completely burned by an engine while NOx emissions occur at elevated engine temperatures when trace substances in the fuel such as ammonia are oxidised. Carbon dioxide is also produced by motor vehicles. It is formed during the complete combustion of fuel. Although not strictly considered a pollutant, as it already exists as a trace gas in the atmosphere, excessive levels of CO2 produced by road vehicles are considered a prime contributor to the climate change mechanism known as the "Greenhouse Effect". (Clifford J, 2007)

A succession of increasingly stringent automotive emission control laws have been introduced by the European Commission in an attempt to reduce the levels of pollutants entering the atmosphere from road vehicles. Fig. 1 shows the reduction in acceptable levels of pollution since 1992 (the quantities are calculated for heavy goods vehicles (HGVs) and are given in g/kWh). (Clifford J, 2007)

The most common sensor used to detect automotive pollution is the Lambda sensor. The Lambda sensor operates by comparing the levels of oxygen in the exhaust with those in ambient air. If the level of oxygen in the exhaust is too low, high levels of CO and HC are produced, it signals to the engine to increase the fuel to air ratio. If the

level of oxygen is too high, high levels of Nox are produced, and it signals to the engine to decrease the fuel to air ratio. However, the Lambda sensor is not designed to quantify the levels of these pollutant gases (or carbon dioxide) leaving the engine as required by European emission laws. An additional difficulty with the Lambda sensor is that it degrades over time on contact with hot and corrosive elements in the exhaust. The net effect of this damage is that eventually the Lambda sensor will produce false readings causing extra fuel to be burnt which not only ruins fuel economy and damages the catalytic converter, but is also responsible for the production of increased levels of pollution. As a result of this the Lambda sensor must be replaced every 30,000–50,000 mile, which is much less than the lifetime of an average vehicle. (Clifford J, 2007)

In contrast to the Lambda sensor, an optical fibre sensor is immune to corrosion by chemicals as it is constructed from glass. Furthermore, the use of optical fibre allows the emitter and detector electronics to be located at a safe distance from the exhaust manifold and the small size and weight of optical fibre ensures that the system will not obstruct the flow of exhaust gases. As each pollutant gas has a characteristic optical absorption spectrum it is possible to determine which gas is present and in what quantity by analysing its unique optical spectrum. Clearly, a gas sensor based on absorption spectroscopy does not suffer from being cross-sensitive to other species present in the exhaust provided its spectrum can be uniquely defined and the spectral resolution of the detector is sufficient. Optical absorption lines occur throughout the electromagnetic spectrum. To date, most optical fibre based sensing has concentrated in the near-infrared due to the greater availability of components designed and optimised for use in the telecommunications industry. However, the fundamental absorption lines of most of the exhaust gases are located in the mid-infrared region with weaker overtones in the near-infrared. Certain pollutant gases such as nitric oxide and nitrogen dioxide have high absorption in the ultraviolet region, in addition to having fundamental

absorption lines in the mid-infrared and in recent years ultraviolet optical fibre gas sensors have been developed to detect these gases. However, the carbon gases, i.e. carbon monoxide and carbon dioxide only absorb radiation in the infrared region. Fig. 2 shows the infrared absorption of carbon dioxide between 0.2 and 5.2 m. (Clifford J, 2007)

Recent improvements in components at the mid-infrared wavelength range have indicated that it is feasible to construct an optical fibre gas sensor suitable for use in a vehicle that operates in this spectral region. Previous mid-infrared optical fibre gas sensing reported in the literature has involved the use of expensive and bulky components such as Helium Neon lasers, Quantum Cascade Lasers, Fourier transfer infrared (FTIR) spectrometers, and cooled InSb detectors, which are not suitable for use in a vehicle. However, recent advances in mid-infrared components have included the improvement in output power of mid-infrared sources, the increased transmission and mechanical durability of mid-infrared fibre and the availability of mid-infrared detectors that do not require thermoelectric or nitrogen cooling have indicated that it should be possible to design an emission detection scheme based on mid-infrared components. Low cost mid-infrared sources such as filament emitters can provide adequate optical power when coupled to optical fibre. Chalcogenide optical fibres, which transmit in the 1–6 _m range, have attenuation losses, which compare quite favourably with other types of fibre available in this wavelength range such as silver halide fibre. Pyroelectric detectors, which do not require cooling, only respond to pulsed infrared signals and are therefore highly suitable for measuring pulsed infrared signals in the hot background exhaust environment. The pyroelectric detector can also be fitted with a narrow band optical filter to make it selective to the absorption line of the gas of interest. (Clifford J, 2007)

2.1.3 Butane Gas Sensor

Liquid petrol gas is widely used in industry and domestic appliances. Metal oxide semiconductor gas sensors have been used for domestic gas leaks detectors in house to produce an alarm at a given gas concentration. Conventional hydrocarbon gas sensors, normally operated above 300–400 °C , require the source of high electric power, and had poor selectivity to the ethanol vapor which is the main interfering gas in domestic ambience. In such places, workers can carry a portable sensor with a small battery for safety. Such sensors need for selective gas with respect to ethanol and operating at a low temperature for a longer battery life is obvious.

Several designs of sensors' construction, SnO_2-based, were proposed for achieving the selectivity, sensitivity and stability of combustion gas detection with respect to ethanol vapour such as directly doping of small amounts of noble metals (Pd, Pt, Rh and Ru) into SnO_2 a suitable filter containing noble metal catalysts method and a directly coating selective thin film on the surface of SnO_2 layer structure.

To develop a low temperature-operating combustion gas sensor, some problems such as reproducibility of output, low sensitivity, selectivity with respect to ethanol and effect of humidity should be solved because of low degree and slow rate of sulphur ions and surface reactions at a low temperature. Butane semiconductor gas sensor with low

operation temperature has been developed based on two-side construction which allows miniaturization of the sensor chip and most active catalyst Co_3O_4.

In the present study we report the butane sensor based on laminating two-layer thick films (SnO_2 as the first layer and alumina-supported Pd catalyst as the second layer). The butane gas sensor based on a two-side construction (right side as sensing and back side as heating) which allows miniaturization of the sensor for operation at low temperature. The operation temperature, thickness of two-layer thick film, response and recovery time and the effect of humidity were investigated for the optimal condition chosen. The sensing characteristics of response linearity and long-term stability were further tested.

2.1.4 Propane and Butane Semiconductor Gas Sensor

Nowadays the semiconductor gas sensors are broadly applied to the atmosphere monitoring system, the toxic or explosive gases detection system, the chemical processing facilities, the intelligent buildings with environmental control functions and so on. One of the most broadly utilized semiconductor gas sensors is the tin oxide based sensor, which is commercialized as a world-famous product by Figaro, Japan. The Figaro sensor consists of the platinum coil heater placed inside the miniature ceramic tube. On the external surface of the tube, tin dioxide sensing layer is placed along with the contact pads contacting thin connection wires. (Kim J.H, 1997)

Even though this structure is very reliable and shows a good stability of the sensor properties, its disadvantage is high power consumption from 400 mW to 1 W due to heating of the massive ceramic tube. This level of power consumption has a limit for the sensors to be adopted in a battery operation portable device. (Kim J.H , 1997)

Through the cooperative research between Institute of Molecular Physics (RRC 'Kurchatov Institute', Russia) and Korea Institute of Energy Research (KIER, Korea), lower power consumption semiconductor gas sensors of thick film type were aimed to develop. As a target the power consumption of the sensors for propane/butane in air is as low as 100 mW. This level of power consumption seems to be good enough for the battery operation portable device which is able to run for about 10 h without recharging the battery. (Kim J.H., 1997)

As the basic technology for the fabrication of sensors the thick film processing was applied. Advantages of the thick film technology are: the possibility of large scale mass production (one can obtain several thousands sensor chips from one substratum) and the possibly automation of all steps of the sensor fabrication. The other distinctive advantage of the thick film technology is the stability characteristics of printed thick film layers. Several steps were undertaken in order to decrease the power consumption and optimize the construction of semiconductor gas sensors. (Kim J.H., 1997)

The used of two-side construction (see Figure 2) which allows miniaturization of the sensor chip. The final dimensions of the sensor chip were as small as 1.5 mm×0.3 mm×0.15 mm. The thickness of the alumina substratum was decreased up to 0.1 μm.

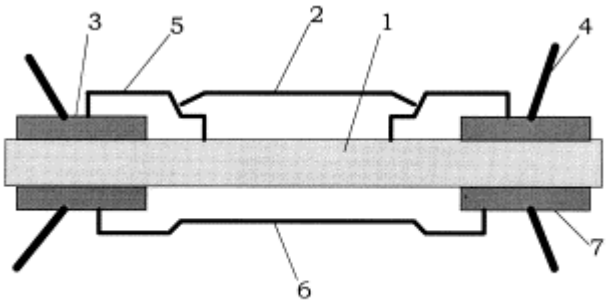

Figure 1: Structure of developed sensor. 1, Alumina substratum; 2, sensing layer; 3, contact pads; 4, connecting wires; 5, disjunction layer; 6, heater; 7, contact pads.

For the preparation of tin oxide powder, an oxalate method with an original preparation process was followed. After the precipitation the powder was dried at 500°C for 2 h. Then, an averaged particle size was observed as about 0.1 μm by SEM pictures as shown in Figure 3 (a) and the specific surface area was measured as approximately 18 $m^2 g^{-1}$ by BET method. (Kim J.H., 1997)

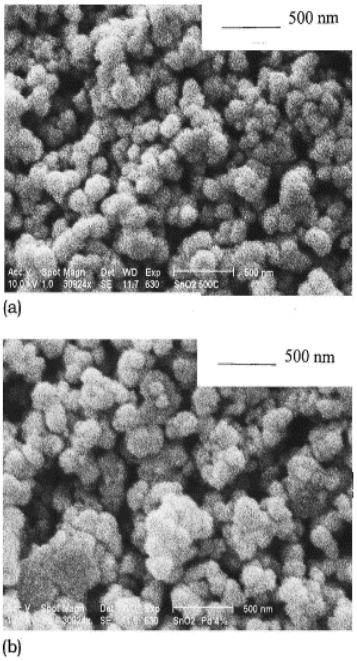

Figure 2: SEM pictures of tin oxide: (a) dried at 500°C and (b) doped with 4 wt% Pd.

To increase the sensitivity, some preliminary investigations on doping of catalytic novel metals were conducted for various combinations of mixing ratio and a few groups of Pd and Pt particle sizes. But in this paper all sensors were restricted to 4 wt.% of Pd doped sensing material. After doping, by means of an organic solution of HCOONa, an averaged cluster diameter was increased about two times compared with the undoped tin oxide powders as shown in (b). The paste for screen printing of the sensing layer mixed with the Pd doped tin oxide powder (60 wt%) and the glass binder (40 wt.%) composed of B_2O_3, SiO_2 and some metal oxides was used. (Kim J.H, 1997)

The composition of the resistive material for thick film heater was developed. The material is based on 65 wt% of ruthenium dioxide and 35 wt.% of the glass binder. As shown in Figure 4 (a) and (b), it was observed as about 0.3 μm of an averaged cluster size before drying the ruthenium oxide and about 0.1 μm of particle size after two steps of drying at 400°C for 2 h and then 600°C for 2 h in order to prevent recrystallization.

The prepared heater material is stable up to temperatures of 600°C. The other advantage of the heater is the possibility to change its resistance by varying the ratio of ruthenium dioxide to the glass binder. Thus, the heater parameters can be adjusted in order to provide the necessary temperature at the requested voltage (i.e. 3 V). (Kim J.H , 1997)

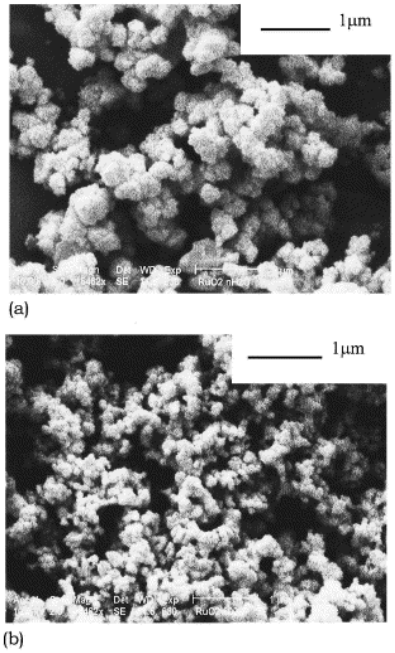

Figure 3: SEM pictures of ruthenium dioxide powder:

(a) Before drying and (b) after drying.

The construction of the sensor was optimized in order to decrease heat losses by heat conduction, radiation and convection. A computer simulation of heat transfer for the sensor was conducted by the computational scheme of the finite elements method. From the results of simulations, the materials and dimensions for contacting wires, contacting pads, the substratum could be optimized to minimize heat losses in the sensor. (Kim J.H , 1997)

Based on the general thick film printing technology, all fabrication procedures including photo mask preparation, screen printing, drying, firing, laser cutting of the substratum to separate printed chips and wire contacting by 20 μm diameter of platinum wire were conducted. (Kim J.H, 1997)

2.1.5 Liquefied Petroleum Gas Sensor

Commercial solid state gas sensors based on semiconducting metal oxides have been marketed during last 50 years, using the property that the sensing gas changes the surface charge carrier concentration of semiconductor to cause changes in its electrical conductivity. This helps to monitor hazardous gases and to detect the threshold level of gases present in the atmosphere. However, these sensors showed poor performance with respect to the sensitivity at low concentrations of gases, selectivity and long-term stability. The gas-sensing devices based on organic materials, such as polypyrrol, polyaniline, and metaphthalocyanines, have gas sensitivity at room temperature, but their long response time (min) due to the orderly structure limits their usage. (Joshi S.S 2007)

As an alternative, heterojunction-based sensors have been constructed. Usually, a heterojunction gas sensor consists of two semiconducting oxides in contact, with enhanced sensing behaviour occurring at the interface between the two materials. Gases that are adsorbed onto the sensor surface on either side of the heterojunction modify its charge-transfer characteristics by changing the structure of the interfacial barrier.

This process gives rise to a gas detection mechanism distinct from that of semiconductor metal oxide sensors. Heterojunctionbased humidity sensors were first proposed in 1979. The responses of different heterojunction-based sensors to a range of gases including CO, H_2, H_2O, NO_2 and C_2H_5OH have been investigated. Several rectifying junctions formed between p-type and n-type semiconducting ceramics include CuO(p)/ZnO(n), La_2CuO_4(p)/ZnO(n) and $SmCoO_3$(p)/Mox(n), where M Fe, Zn, In, Sn. In addition, n-type semiconductor heterojunction ceramics with slightly different band energies have also been reported, e.g., a NO_2 gas sensor based on SiC and ZnO has been investigated. Since the resistance of the SiC component of the heterojunctionwas unaffected by the introduction of NO_2 and that of the ZnO component was only slightly affected, it was concluded that the increase in electrical resistance associated with the introduction of the NO_2 was due to the sulphur of the n n junction interface. A CO gas sensor was prepared by co-firing n-type ZnO and SnO_2 layers. Heterojunctions based on semiconductor oxides usually employ high temperature and low-pressure techniques to fabricate it. (Joshi S.S 2007)

Recently, conducting polymers find place as gas sensors because of easy synthesis and room temperature operating devices. Among several polymers studied, polyaniline presents advantages for applications in electronic devices since its electrical properties can be changed by oxidation or protonation in the imine nitrogen backbone, and additionally it presents thermal and environmental stability. Polyaniline-based solidstate devices are of low cost and useful in electronics, storage devices and sensors. Polyaniline and its nanocomposites have been fabricated in bulk form using electrochemical polymerization. Poylaniline–SnO_2 hybrid material has been prepared by a hydrothermal route. Similarly polyaniline has been processed into thin film form using different methods including spinning, vacuum sublimation, Langmuir–Blodgett

(LB) techniques. These films have been used for the detection of H_2S, SO_2, NH_3, methanol, acetone, etc. and in biosensors as well. (Joshi S.S 2007)

Laranjeira et al. have fabricated a high quality Si–polyaniline junction for sensing radiation (γ) and ammonia gas. Survey of gas sensor literature revealed applications to sensing almost all hazardous gases, including liquefied petroleum gas. This includes the use of polymers to detect and measure the concentration of gaseous pollutants as sulphur oxide, nitrogen oxide and toxic gases. The sensitivity to some reducing gases (acetone, ethanol, methane and liquefied petroleum gas) of calcia-doped nickel ferrite ($NiFe_2O_4$ + 1% CaO) and cobalt and manganese-doped nickel ferrite, $Ni0.99Co0.01MnxFe_2{-}xO_4{-}\delta$ (x = 0.01 and 0.02), was investigated by Rezlescu et al. In a temperature range of 378–558 K. (Joshi S.S 2007)

Being highly explosive, leaking of LPG is a serious problem. Consequently, there is a need for development of cost effective sensors to monitor LPG of the lowest possible concentration at room temperature. The present work, for the first time, describes a technique to form an n-CdSe/p-polyaniline heterojunction with a good rectification ratio. These characteristics in part are a requirement for further use of the devices in a variety of sensor applications. The n-CdSe/p-polyaniline heterojunction in thin film form has been fabricated using simple electrodeposition technique. Before fabricating the junction, the individual films were characterized by XRD, SEM and AFM techniques. The forward bias current–voltage characteristics of the junction at room temperature were recorded before and after exposure to LPG at concentrations in the range of 0.02–0.10 vol%. (Joshi S.S 2007)

Table 1: Summary of the literature review

Research	Method	Finding
• Propane/butane semiconductor gas sensor with low power consumption (Kim J.H, 1997)	• semiconductor resistive	• Sensitivity, as the relative change of the sensor conductance with respect to reference standard air, is around 14 at 100 mW of optimal heater power. • The response time in the 7 RH% and 0.6 vol.% of propane air mixture are about 10 and 150 s of the recovery time in terms of the 90% fall and rise time.
• Detection of carbon dioxide emissions from a diesel engine (Clifford J, 2007)	• mid-infrared optical fiber	• Its detection limit of 350 ppm is sufficiently low to be adequate for this task as carbon dioxide emissions from modern diesel engines still exceed 1%.
• Liquefied petroleum gas sensor (Joshi S.S 2007)	• semiconductor	• This sensor sensed the liquefied petroleum gas (LPG) at room temperature (300 K). • The maximum response was found to be 70% at a LPG concentration of 0.08 vol%. • The response time was ranged between 50 and 100 s, whereas the recovery time was 200 s.

2.2 Sensing Element

2.2.1 Lanthanum (III) Oxide

Lanthanum (III) oxide is La_2O_3, a chemical compound containing the rare earth element lanthanum and oxygen. It is used to develop ferroelelectric material, and in optical materials. Production is on laboratory scale, mostly. At low temperatures, La_2O_3 has an A-M_2O_3 hexagonal crystal structure. The La^{3+} metal atoms are surrounded by a 7 coordinate group of O^{2-}atoms, the oxygen ions are in an octahedral shape around the metal atom and there is one oxygen ion above one of the octahedral faces (Wells 546). On the other hand, at high temperatures the Lanthanum oxide converts to a C-M_2O_3 cubic crystal structure. The La^{3+} ion is surrounded by a 6 coordinate group of O^{2-} ions (Kale 2005).

La_2O_3 is used to make optical glasses, to which this oxide confers increased density, refractive index, and hardness. Together with oxides of tungsten, tantalum, and thorium, La_2O_3 improves the resistance of the glass to attack by alkali. La_2O_3 is an ingredient for the manufacture of devices for piezoelectricity, galvanothermy, and thermoelectricity material. Automobile exhaust-gas converters contain La_2O_3 (Cao 408). La_2O_3 is also used in X-Ray imaging intensifying screens, phophors as well as dielectric and conductive ceramics.La_2O_3 has been examined for the oxidative coupling of methane (Maoilova 1980).

La_2O_3 films can be deposited by many different methods, including: chemical vapor disposition, thermal oxidation, sputtering, and spray pyrolysis. Depositions of these films occur in a temperature range of 523–723 K (Kale 3007). Polycrystalline films are formed at 623 K (Kale 2005).

2.2.2 Iron (III) Oxide

Iron(III) oxide also known as ferric oxide, Hematite, red iron oxide, synthetic maghemite, colcothar, or simply rust is one of the several oxide compounds of iron, and has paramagnetic properties. Its chemical formula is Fe_2O_3 (N. N. Greenwood).

Iron (III) oxide is often used in magnetic storage, for example in the magnetic layer of floppy disks. These consist of a thin sheet of PET film, coated with iron (III) oxide. The particles can be magnetized to represent binary data. MICR (Magnetic Ink Character Recognition) also uses iron (III) oxide compounds, suspended in an ink which can be read by special scanning hardware. The majority of recorded information on earth (such as text and photographs) is stored in the form of magnetization patterns on a thin layer of iron (III) oxide. This is probably because the cost per bit of iron-based magnetic media is currently far less than the cost per bit of any known alternative, such as optical discs, paper books, or microfilm.

More text and photos are stored on magnetic media than all the paper books and paper photographs in the world. Iron (III) oxide is used in the production of pure iron in a blast furnace. Iron (III) oxide is also used in an extremely exothermic reaction called a thermite reaction. It also can use as sensor for LPG. (Adlam & Price 1)

CHAPTER 3

METHODOLOGY

3.1 Pellet Fe_2O_3 and La_2O_3 using hydraulic press

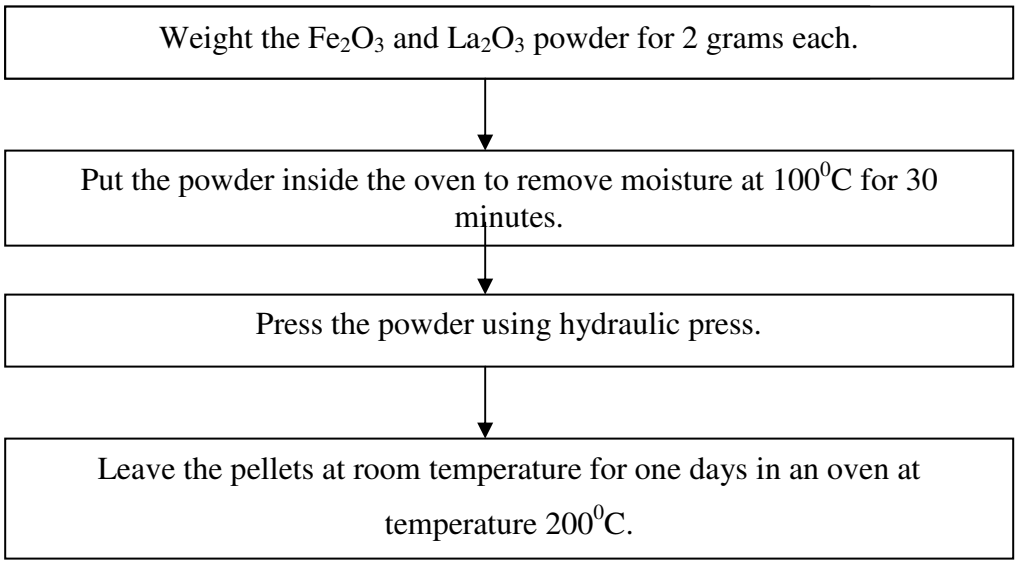

Figure 4: Flow of pellet process of Fe_2O_3 and La_2O_3

Two chemical have been selected according to their properties which are Fe_2O_3 was negative substrate and La_2O_3 was positive substrate. These two chemicals are also easy to get and cheap compare to other chemical. Then after selected the desired chemical, the chemical have to change their form from powder form into pellet form. In order to change their form, hydraulic press has been used. Two grams of each chemical were weight. After that the chemical were placed in the oven for 30 minutes at 100^{o}C to remove the moisture. Then press the pellet using hydraulic press. The size of the pellet was 1cm in diameter each and 0.5cm thickness. A schematic drawing of the hetero-junction is shown in Fig. 5. It consists of a stainless steel substrate onto which Fe_2O_3 and La_2O_3 substrate are subsequently deposited (1 cm^2 area).

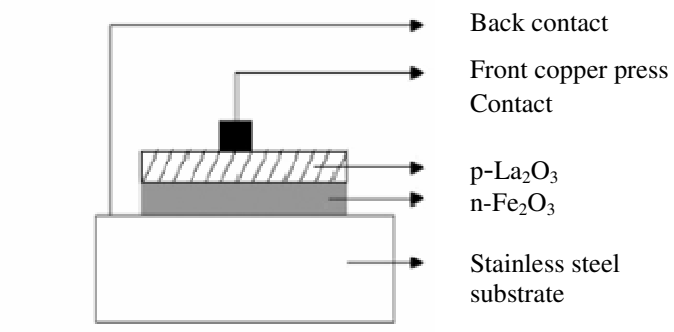

Figure 5: A schematic drawing of n-Fe_2O_3/p-La_2O_3 hetero-junction

3.2 Thermogravimetric Analysis

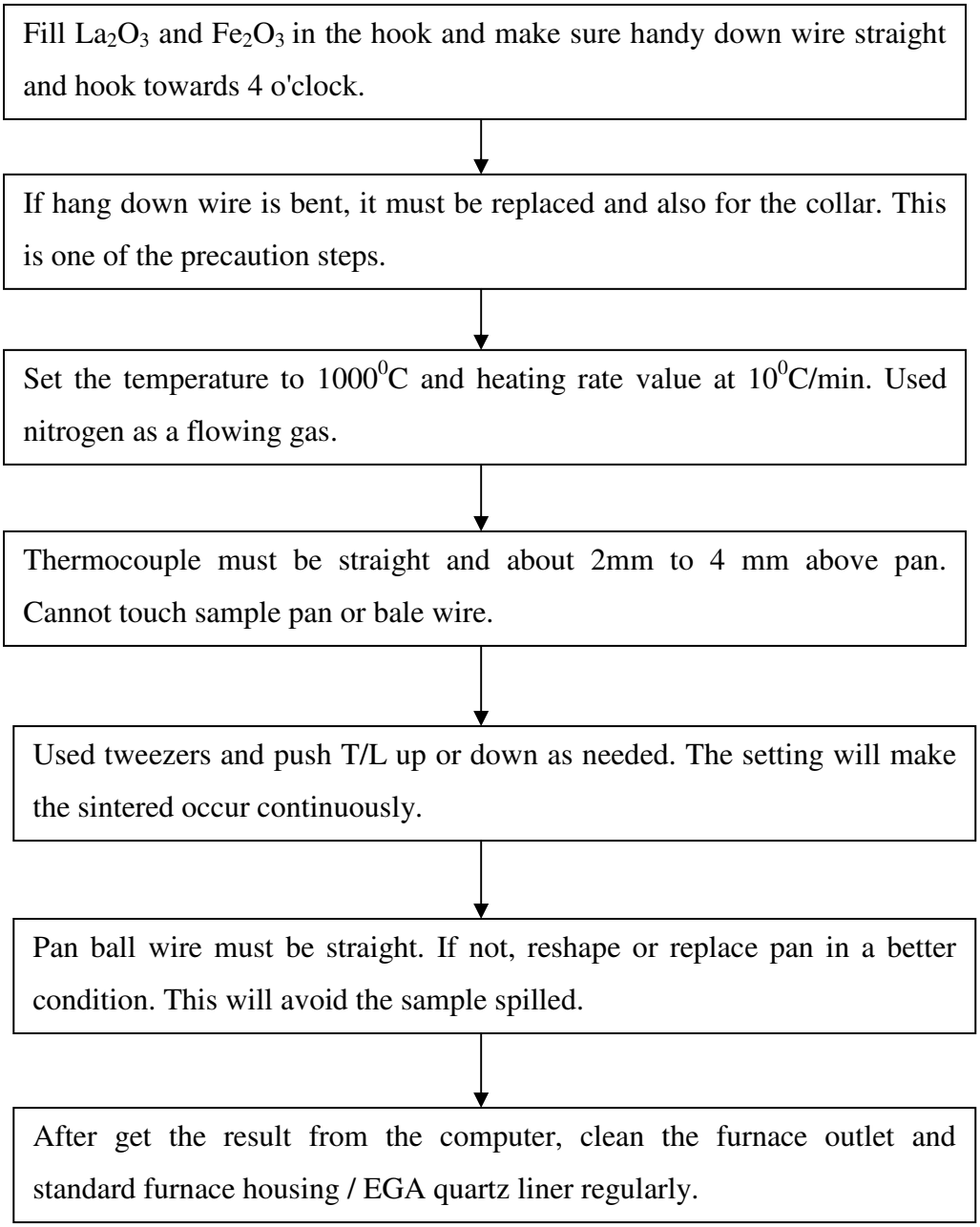

Figure 6: Flow of using Thermogravimetric Analysis

Thermogravimetric Analysis is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Sample will be placed in the collar. After that, setting their required setup such as temperature at 1000^0C, heating rate at 10^0C/min and flowing gas used is nitrogen. After setup their setting and followed the precaution step, this machine will automatically move the collar inside the furnace and then sintered the sample following the setting.

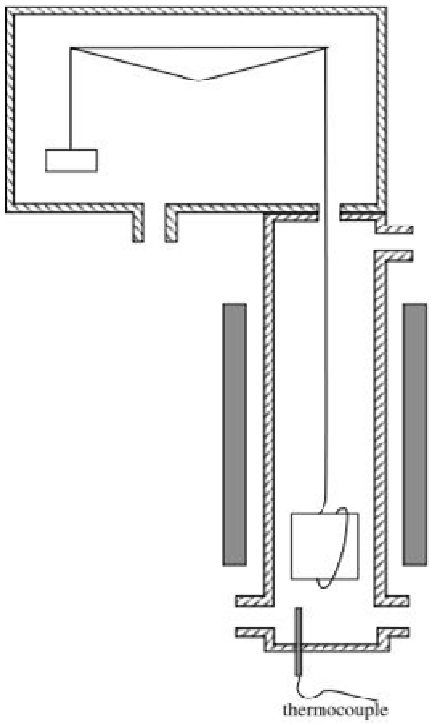

Figure 7: Sketch of typical TGA

3.3 Testing of LPG sensing properties of p-La_2O_3 /n-Fe_2O_3 junction

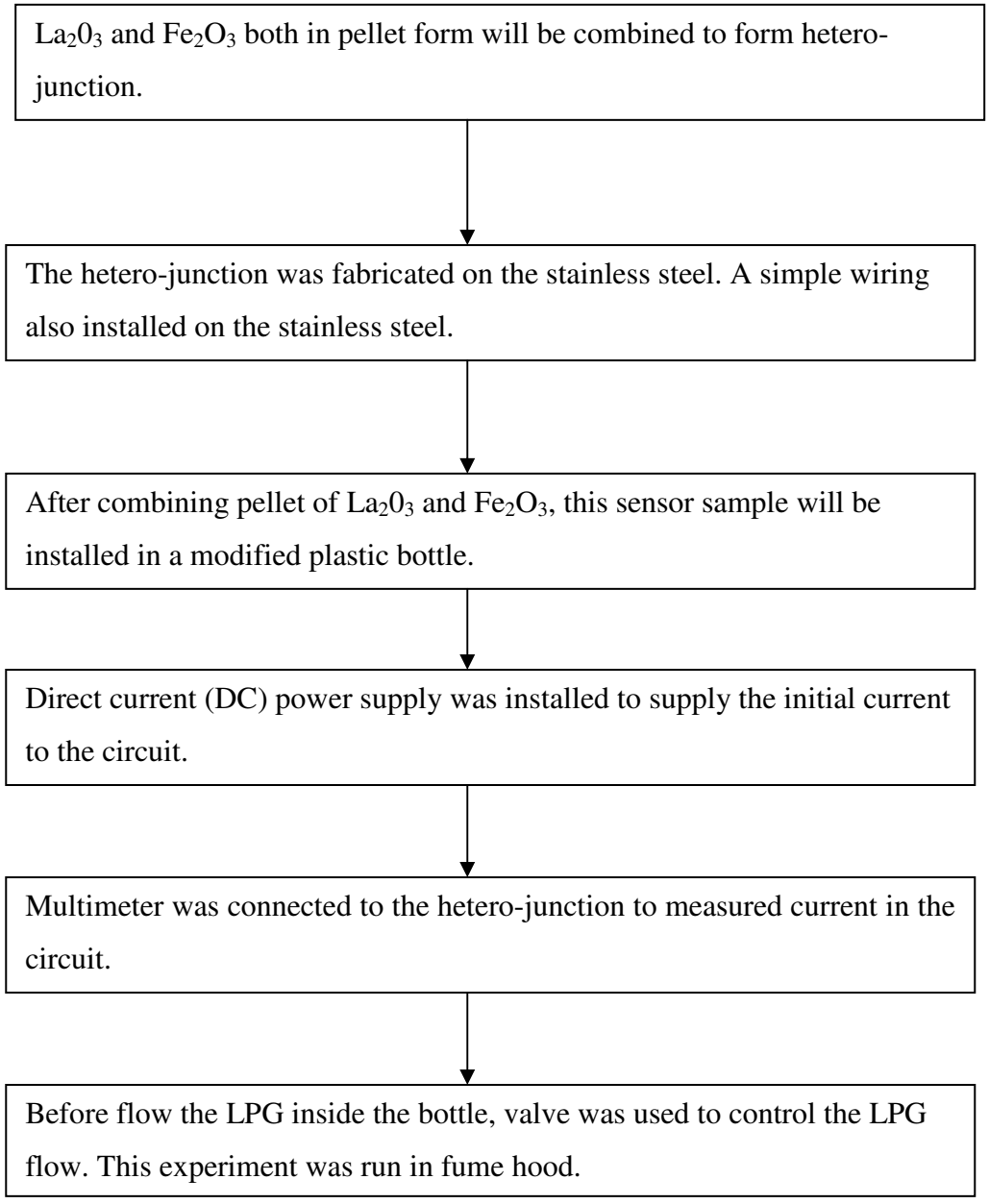

Figure 8: Flow of Testing of LPG sensing properties of n-Fe_2O_3/p-La_2O_3 Junction

The gas sensor unit consists of a small dome-shaped modified plastic bottle. The special mounting for the sample was permanently installed inside the plastic bottle. Through the external connections, current of the circuit were recorded using a multi meter. Direct current (DC) power supply has been used to supply initial current to the circuit which is 1 µm. An integral bonet needle valve with tubing size 1.4 inch has been installed at the gas inlet to control LPG flow rates from commercial LPG tank. This experiment was run in the fume hood to avoid LPG from spread to the air.

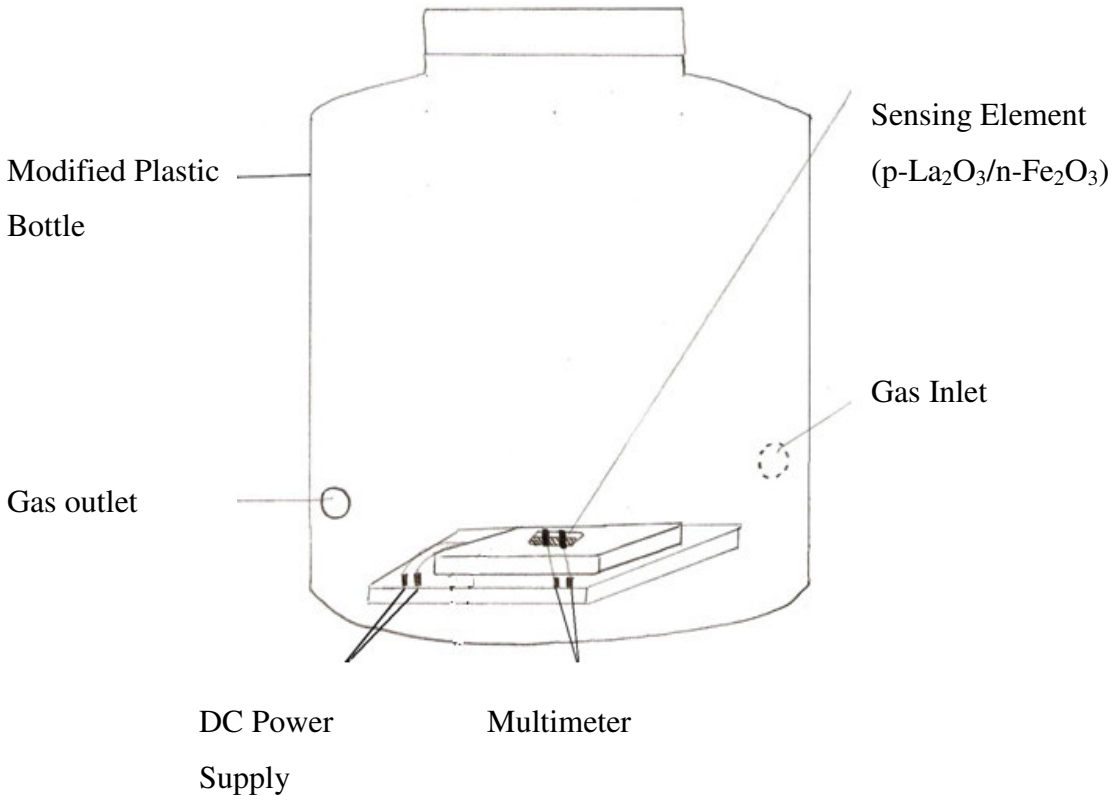

Figure 9: A schematic view of gas sensor unit

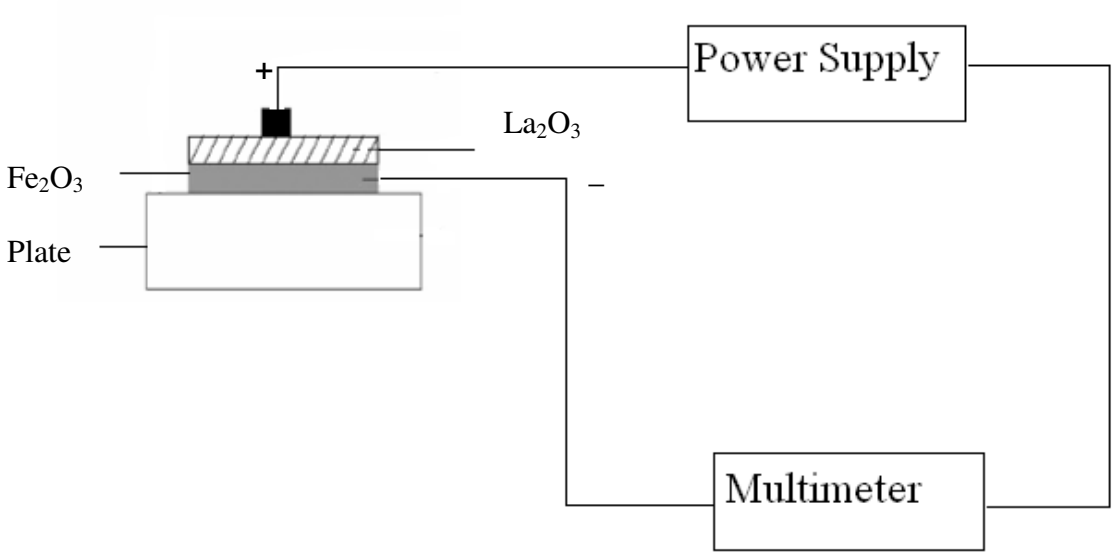

Figure 10: Schematic diagram for LPG sensor circuit

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization

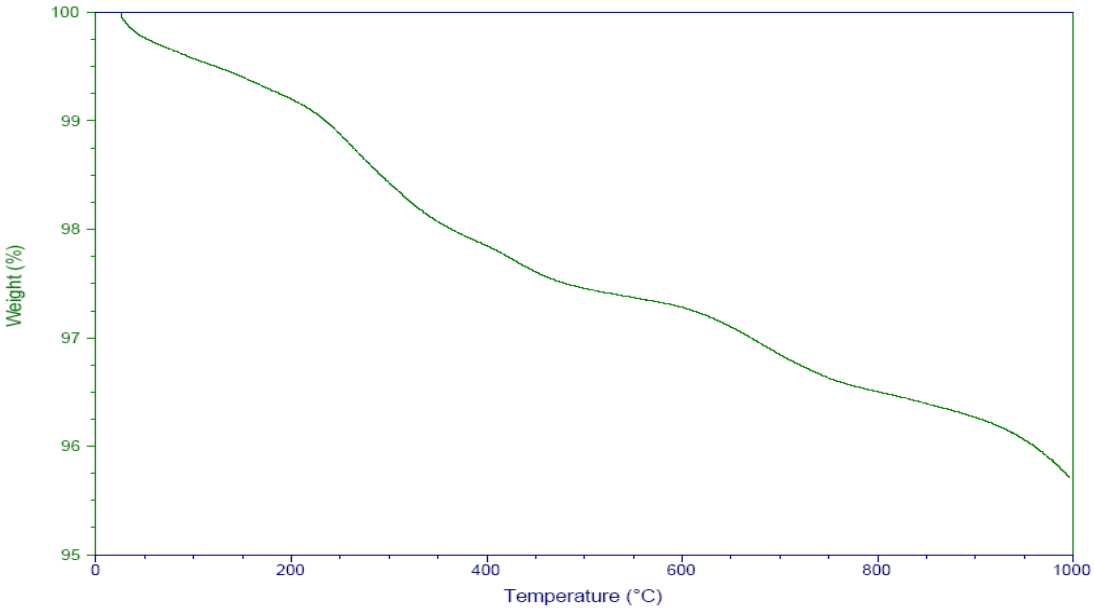

Figure 11: Thermo gravimetric analysis of Fe_2O_3

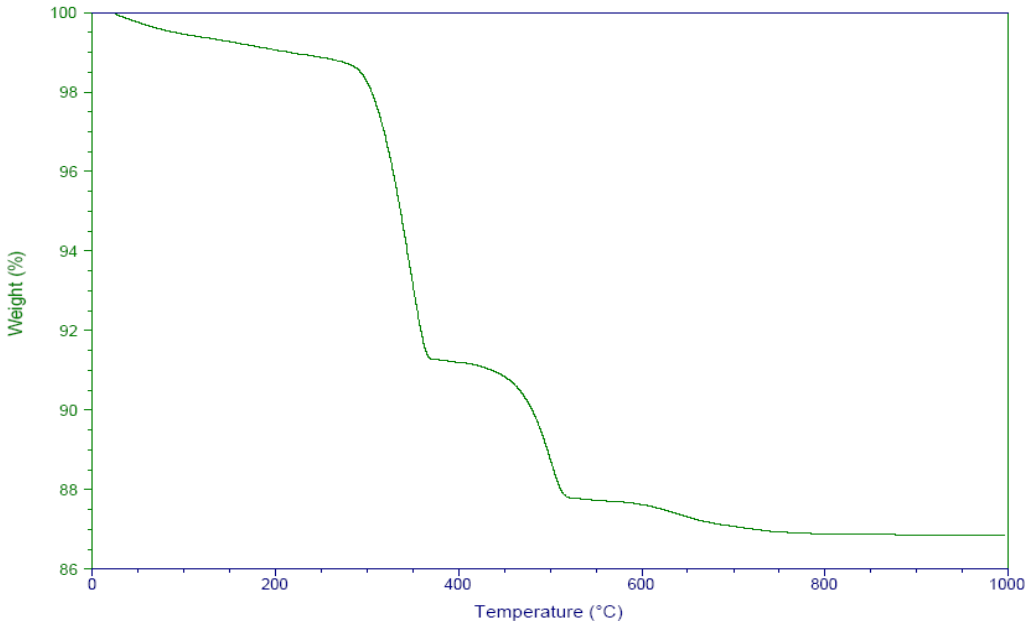

Figure 12: Thermo gravimetric analysis of La_2O_3

Figure 15 and Figure 16 represent the mass drop and thermal stability of Lanthanum Oxide and also Iron (III) Oxide.

Thermogravimetric Analysis or TGA is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

Thermo gravimetric Analysis (TGA) has been done in this research to study on the thermal stability of lanthanum oxide and iron (III) oxide. TGA will be shown the drop of mass as temperature is increasing. The medium of combustion was used nitrogen because of their special properties. Nitrogen is almost inert gas and will not disturb the heating process. Nitrogen also will cause incomplete combustion that will cause the process to be pyrolysis process. Heating rate for the sintered process was choosing 10^0C/min. This value was selected because this chemical needed to sinter slowly to study on temperature not on heating rate. If we set higher heating rate, it will cause the chemical increasing the temperature rapidly and will made mass drop happen radically.

From the Figure 16 show that mass drop when increasing of temperature. This graph show the stability line of lanthanum oxide when temperature reaches at 800^0C. At this condition lanthanum oxide will be oxidize into another oxide either LaO or LaO_2. The exact oxide of lanthanum can be known using X-ray diffraction (XRD). This XRD is an efficient analytical technique used to identify and characterize unknown crystalline materials. In the earlier heating in range 0^0C to 150^0C, water and other moisture will vaporized and that is the reason of mass reducing. The decreasing of mass occurred rapidly in temperature between 300^0C to 350^0C**.** After that the mass will maintain at the same stage shortly and will decrease back.

In Figure 15, for 1000^0C still cannot change the original form of iron (III) oxide. In the earlier heating in range 0^0C to 150^0C, water and other moisture will also vaporized and that is the reason of mass reducing. Furthermore, the decreasing of mass in Figure 15 shows at constant rate. The graph also did not show any straight line or

stability line. So from the graph we know that iron (III) oxide will remain as iron (III) oxide in the end of the sintered process.

4.2 Performance

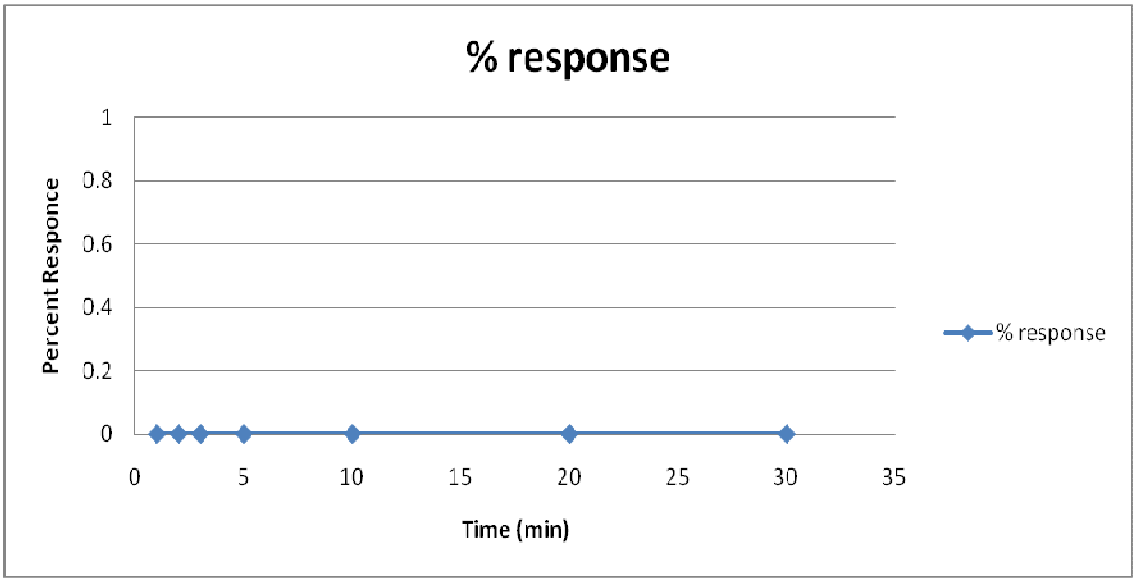

Figure 13: Detection using p-La_2O_3 and p-La_2O_3

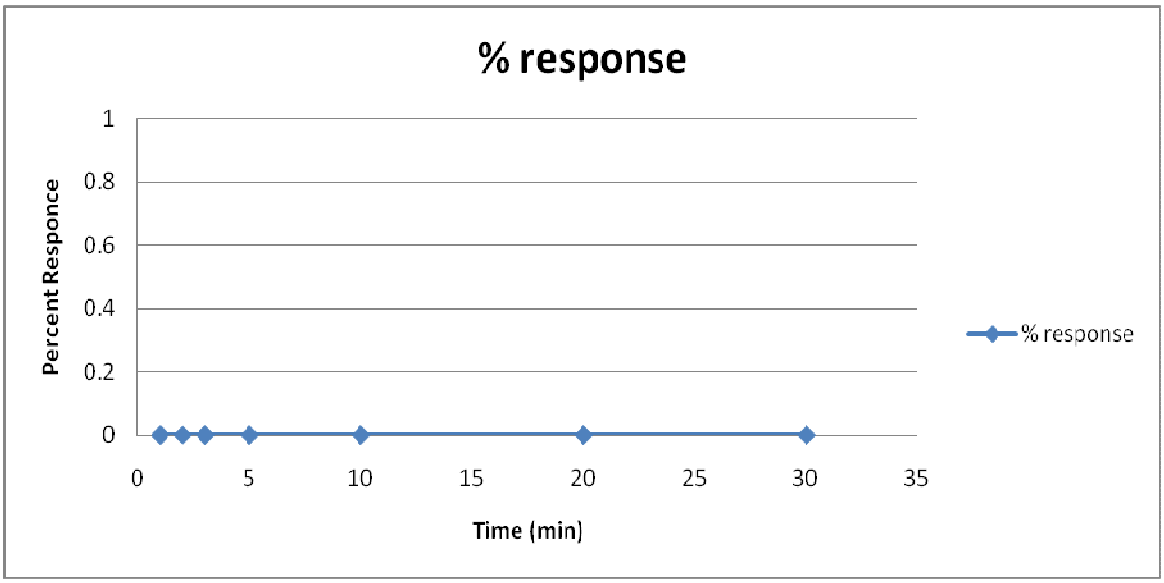

Figure 14: Detection using n-Fe_2O_3 and Fe_2O_3

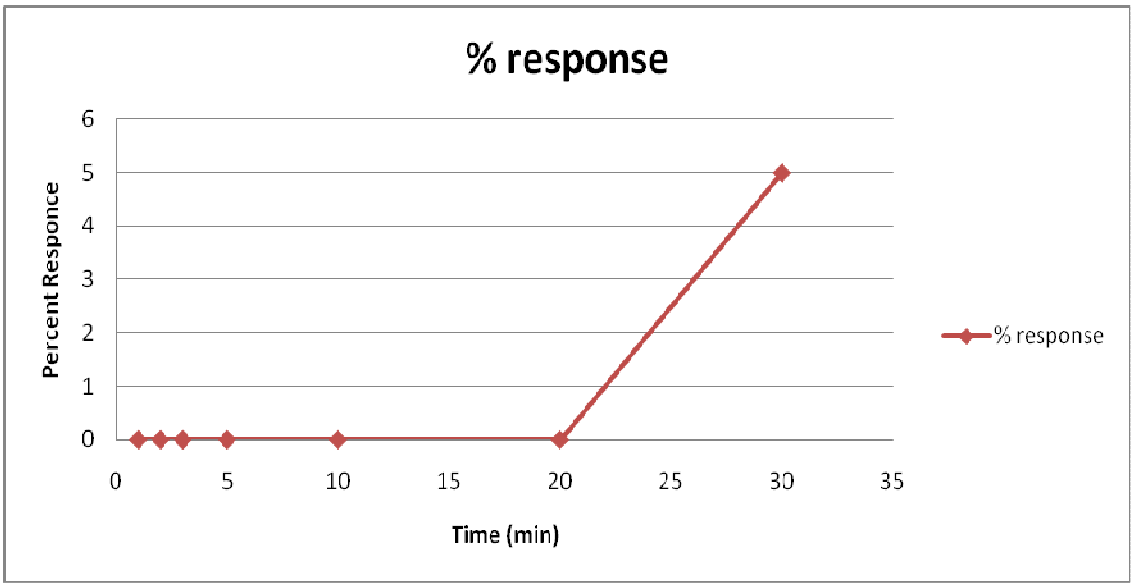

Figure 15: Detection using La_2O_3 and Fe_2O_3

From Figure 12 and Figure 13, the detection of LPG within first thirty minute using p-La_2O_3 and p-La_2O_3 and n-Fe_2O_3 and Fe_2O_3 combination is failed. In Figure x3, show that is some response to the LPG after using p-La_2O_3 and Fe_2O_3 as sensing element. Even the detection only occurred in last minute, but this experiment still achieves the objective which is to detect the LPG in room temperature.

The measurements of current of the hetero-junction were performed at room temperature in the absence and presence of LPG. As soon as the hetero-junction was exposed to LPG, the forward current increased sharply with an increase in concentration of the LPG. The increase in current with the sensing LPG has been attributed to the increased conductivity and/or the change in work function of La_2O_3. The LPG response of the sensing element is calculated using equation;

$$\text{Response } (\%) = \left(\frac{\Delta I}{Io}\right) \text{ x } 100\%$$

Where ΔI the change in current is after exposure to LPG and I_0 is the current before exposure.

During the experiment, current of circuit were set to 1μA. The current have been measured using multimeter. After hetero-junction exposed to the LPG for 1, 2, 3, 5, 10, 20 and 30 minutes, the existing of LPG will be measured or detected when there is response in multimeter. After only twenty minutes, the multimeter shows some differential of initial reading. The increasing of the reading continuously occurred and at thirty minutes the reading of the multimeter were 1.05 μA. So after calculating using equation 1, the percent response was about 5%.

This research has run three experimental on the detection of the LPG which is using p-La_2O_3/p-La_2O_3, n-Fe_2O_3/n-Fe_2O_3 and p-La_2O_3/n-Fe_2O_3. When used combination of p-La_2O_3/p-La_2O_3 and n-Fe_2O_3/n-Fe_2O_3 the result will shown in Figure 1and Figure 2. The graph shows that there was no response because of the positive substrate and negative substrate on either side. The positive substrate is also known as a receiver. So when both of it was receiver, there will never achieve stability. Same goes

to the negative substrate, it is a donor type. So when both of them donated the electron, there will not achieved stability. Furthermore, when there was did not achieved the stability that mean there will be no current can through them. That is why there is no detection because of the circuit did not complete as a loop.

For the last combination which is between p-La_2O_3/n-Fe_2O_3 the result was shown in Figure 14. From the figure, there some detection at the last of the experimental period which is in between twenty minutes to thirty minutes. The time response was too long. A journal from S.S Joshi, that have been as a main references in this project, LPG will be detected in ranged between 50 and 100s. From the journal they are using p-polyaniline/n-CdSe as their sensing element. After comparing the properties of p-polyaniline/n-CdSe junction with this project which is p-La_20_3/n-Fe_2O_3 junction, there were differences between them. So the reason for the delayed response was because of the properties of the sensing element.

The first main properties that influence the detection are electric conductivity. Electric conductivity or specific conductivity is a measure of material's ability to conduct an electric current. When an electrical potential difference is placed across a conductor, its movable charges flow; it will be giving rise to an electric current. Polymer and metal oxide have high electric conductivity while semiconductor have intermediate electric conductor and insulator has low electric conductivity. So for this research the combination was intermediate and high electric conductivity while for the references journal was high and intermediate. The positive substrate play huge rule compared to the negative substrate. So the advantage was to the combination of polyaniline and CdSe. Beside that that the value of electric conductivity of polyaniline was higher than lanthanum oxide which is 100 S/cm compared to 75 S/cm.

The other difference in their properties is dielectric constant, ε. Dielectric constant is a measure of material under given conditions of the extent to which it concentrates electrostatic lines of flux. It is the ratio of the amount of stored electrical energy when a potential is applied, relative to the permittivity of a vacuum. The dielectric constant for polyaniline is higher than lanthanum oxide. Polyaniline has dielectric constant value of 53pF/m while lanthanum oxide just have 27pF/m. The difference of value is almost doubles. So it is also effect the long response time of lanthanum oxide to the LPG.

Lanthanum oxide has p-type semiconducting properties because its resistivity decreases with an increase in temperature, average room temperature resistivity is 10^3 Ω cm. Polyaniline also p-type but it is polymer. Polymer has average room temperature resistivity lower than a semiconductor. Polyanilne only have 500 Ω cm.

After all, to conclude the properties of the lanthanum oxide and Iron (III) oxide with polyaniline and cadmium selenide, the table below was constructed:

Table 2: The properties of La_2O_3, Fe_2O_3, Polyaniline and CdSe

Properties	La_2O_3	Fe_2O_3	Polyaniline	CdSe
Electric Conductivity	Intermediate	High	High	Intermediate
Dielectric Constant	27pF/m	-	53pF/m	-
Type of material	Semiconductor	Metal oxide	Polymer	Semiconductor
Charge	Positive	Negative	Positive	Negative
Average Room Temperature Resistivity	1000Ωm	-	500Ωm	-

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

It is conclude that p-La_20_3 /n-Fe_2O_3 can sense liquefied petroleum gas at room temperature. The response time will started from approximately at 20 minutes. The response will only occur if the hetero-junction that use is difference substrate. The same substrate will show no detection on liquefied petroleum gas.

Thermo gravimetric analysis of lanthanum oxide will show that the original form of Lanthanum oxide will be transform into another type of oxide such as LaO or LaO_2.

Iron (III) oxide has been remain their original state of oxide even has been sintered in temperature 1000^0C. So it can conclude that iron (III) oxide did not influence by the temperature below than 1000^0C.

5.2 Recommendations

The main recommendation for this research is to change the chemical to be selected as a sensing element. Lanthanum oxide and iron (III) oxide has been proved that will cause a late detection of liquefied petroleum gas.

If those chemical will remain the same, lanthanum oxide should be sintered in higher temperature to strengthen their structure. In this research the chemical only sintered for 200^0C in an oven. So this temperature still cannot improve the structure of lanthanum oxide and it is still too brittle. Lanthanum oxide should be sintered in a furnace at temperature at least 550^0C. If the lanthanum oxide has enough strength, study on the thickness of the pellet can be done.

Concentration of LPG is also important to study on. So study on concentration is also recommended. It is because the flammability of LPG is in between 2% to 10% of concentration in air. So if the concentration within that range and the gas sensor still cannot detect it, explosion can happen if there is some ignition. So it is important to study on the concentration.

Last but not least, the experimental rig should been fabricated well. The plastic bottle can be replaced by glass chamber. This glass chamber should be transparent and can stand with high temperature.

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APPENDICES A

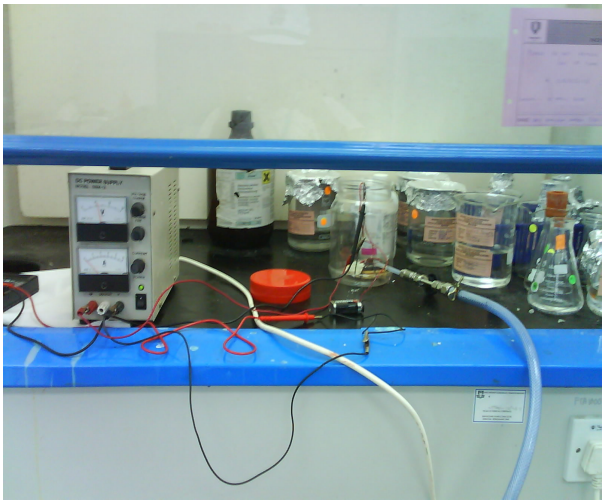

Figure A1: Photo of experimental during experiment inside the fume hood

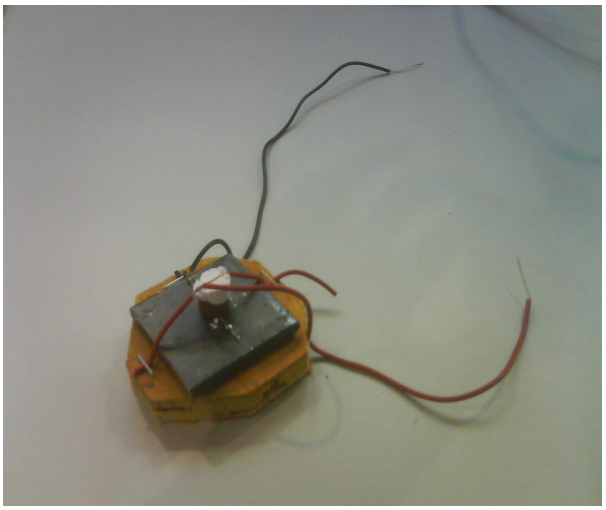

Figure A2: Photo of hetero-junction fabricated on stainless steel

Figure A3: Photo of Thermo gravimetric analysis sample

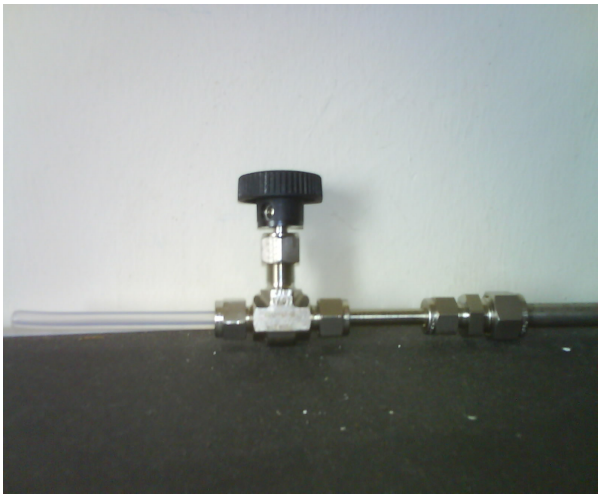

Figure A4: Photo of Integral bonet needle valve

Figure A5: Photo of Fe_2O_3 in powder form

Figure A6: Photo of Hydraulic Press equipment

Figure A7: Photo of La_2O_3 and Fe_2O_3 in pellet and powder form