CHAPTER I

INTRODUCTION

1.1 General Background

Development of gas sensors have proceeded rapidly during the last decade, in response, primarily, to a large R & D expenditure commitment in order to enable environmental legislation to be satisfied [1]. There are two significant factors that will stimulate future gas-sensor device development. Firstly, there is the concern to monitor environmental pollution as well as safety in homes and industrial complexes [2]. Secondly, there is a desire for sensors to monitor process and product performance [1].

The utilization of solid state gas sensor devices in practical applications have resulted in dramatic improvements in industrial process control, in the functioning and facilities of domestic devices, and in the control of environmental pollution through, for example, vehicle exhaust emission controls [3]. However, notwithstanding their success for improved environmental protection, improved process operation or improved product performance, these sensors have not been generally considered sufficiently reliable or durable for industrial flammable gas monitoring [1]. Without developing inexpensive but reliable and durable gas sensors, significant advances in control and instrumentation, which may bring large commercial opportunities and environmental benefits, will not be possible. Unlike the control electronics, the sensor interacts with, and often is exposed to, the environment [4].

A semiconductor chemical sensor may be defined as an electronic device designed to monitor the content of particles of a certain gas in surrounding medium [5]. In a broader sense, chemical sensing involves recording the concentration of particles such as atoms, molecules or ions in gases or liquids using an electric signal [4]. The term 'sensor' and 'transducer' are often used synonymously. According to Ihokura and Watson [6] a 'transducer' is a device that converts one form of energy into another, and a 'sensor' is a form of transducer that converts a physical or chemical quantity into an electrical quantity for purposes of measurement. Terminologically, the active part of a complete gas sensor assembly is called the sensor element, whilst a complete instrument incorporating such a sensor can take the form of a gas monitor, gas detector or gas alarm.

The operational principle of a gas sensor is based on transformation of the value of adsorption of a gas on the surface of the semiconductor directly into an electrical signal [3]. This signal corresponds to the amount of particles adsorbed from surrounding medium or deposited on the surface of operational element of the sensor due to heterogeneous chemical reaction. The high sensitivity of the electrophysical characteristics of these semiconductor materials to adsorption of various gases as well as the capability to control it makes these materials attractive for manufacturing gas sensitive electronic transducers. Gas sensor science and technology draws on various diverse academic fields such as materials science [3], ceramic fabrication [7], solid state physics and surface chemistry [8], electrochemistry [9], catalysis and gas dynamics [8], and solid state ionics [10]. Therefore, the science of chemical sensors generally requires multidisciplinary approach: choosing the physical detection mechanism and the materials; understanding the physical and chemical properties of the interfaces; selecting device technology and eventually studying signal processing.

The Principal types of solid state gas sensors commercially available today are the galvanic oxygen sensors, the catalytic gas detectors and semiconductor oxide sensors [1]. The galvanic and catalytic gas detectors incorporate noble metals such as palladium (Pd) into the device for sensing purposes. Pd is also used as an additive in metal oxide based semiconductor gas sensors in order to improve its sensitivity especially to hydrocarbons. Pd is an element that resists corrosion, dissolves in acids and fused alkalis, readily absorbs hydrogen gas and has a melting point of 1552°C [11]. Semiconductor gas sensors are usually based on the surface properties of the oxides of tin or zinc (SnO_2 or ZnO) [12,13]. These semiconducting oxides could be used for the detection of combustible and toxic gases in air [14]. Their advantages are high sensitivity, simple design, low weight and cost, while, on the other hand, selectivity and stability limit the range of applications. An improvement of these properties cannot be achieved simply by trial and error, but requires a better understanding of the surface processes connected with the conductance changes. In many ways it would be an advantage if the initial studies of the material could be carried out with it in sensor device form [15]. This is not, however, always practicable, since overcoming sensor fabrication problems can be very time consuming. The initial studies, therefore, often involve an investigation of the material properties. Having established the potential of the material as the basis of a gas sensor, device fabrication can then be undertaken in order to establish its feasibility. This is the approached followed in this study.

Tin (IV) oxide (SnO_2) based sensor materials are dominant in research and applications [14,16,17]. Sintered layers and thin films are in practical use. In addition, the surfaces of single crystals are also studied under well-defined conditions to try to achieve a better separation of parameters influencing the properties of gas sensors. Some of the physical properties studied include bulk properties, grain boundary properties and surface properties [18]. In this study, therefore, polycrystalline SnO_2 with Pd as a sensitizing additive is selected as the base material and its electrical properties are analyzed and evaluated with respect to its sensing characteristics to the flammable gas CH_4 in air.

1.2 Scope of the study

Semiconductor gas sensors based on SnO_2 and other metal oxides have not yet attained their projected utility [19]. Although present day sensors respond to part per million (ppm) levels of reducing gases, irreproducibility, drift, and poor selectivity characterize their response. Realizing that any improvement in the gas detection characteristics of metal oxide based semiconductor materials depend on our knowledge of the operating principles of these devices, we embark on an investigation of the characteristics of these devices under controlled environment. In general, the investigation of the sensing properties of metal oxide based semiconductor elements and devices have been of two types. The first, are those researches embracing a wide range of diverse phenomena, and the second are those limited to a thorough study of a particular observation. The flexibility of the first approach prevents the systematic study necessary for a quantitative description of gas sensing characteristics of the materials. The later approach is generally so rigorously limited that it loses sight of the complexity of behavior found in each catalytic material. As a result, there is an insufficient body of quantitative and systematic information concerning the sensing characteristics of metal oxide based semiconductor gas sensors. The scarcity of well-measured electrical response of semiconductor materials to target gases is also another bottleneck limiting the development of descriptive theories of device behavior.

A major concern of this study is, therefore, to acquire a qualitative and quantitative description of the diverse operating characteristic of SnO_2, with Pd as a sensitizing additive, in the detection of CH_4 in air. These operating characteristics include the sintering temperature, operating temperature and the composition of the samples. SnO_2 is chosen as the base material in this study for its proven sensitivity as a gas detector and its chemical stability and durability [13,20]. The behavior of sensor elements and devices based on SnO_2 is characteristic of many sintered and thin film metal oxide semiconductors [20]. What ever has been published in the literature cover limited parameters of the performance of this material in CH_4 detection in a controlled environment. Sensor elements composed only of SnO_2 have a limited sensitivity to chemically stable gases such as CH_4 [13]. Because the gas sensitivity is closely related to redox reactions of the detected gases on the sensor surface, it is reasonable to suppose that it could be improved by including additives which act as catalyst to these reactions. Noble metals such as Pt, Pd, Rh and Ir are very active for oxidation reactions [8]. Therefore, Pd is used in this study as a sensitizing additive that is added as an impurity to SnO_2 to enhance its sensitivity to CH_4. The research will cover higher composition of Pd (up to 15 wt%). Previous studies have concentrated on lower composition of Pd up to about 5 wt% [6]. It is intended, as one of the major objectives of the study, to design a gas sensor test chamber and build a testing rig by which the parameters of the study can be controlled or varied as required.

There are other factors that may influence the sensitivity of gas sensor elements. Some of these factors include the flow rate of the carrier gas and the applied voltage to the sensor elements. The characterization system for this study was designed in such a way that these variables could be controlled or varied as required. Since changes in the partial pressure of oxygen in the carrier gas passing over the sensor element affects its sensitivity [6,8,9,13], it is reasonable to postulate that the flow rate of the carrier gas may affect the oxygen partial pressure and thereby influence the sensitivity of the sensor element. The sensitivity of a sensor element can also be affected by the magnitude of the applied electric field to the sensor element that causes the energy barriers between adjacent grains in the polycrystalline SnO_2 based sensor element to decrease [7].

Another factor that is important in the qualitative and quantitative analysis of gas detection by SnO_2 based sensor elements is the mechanisms underlying the detection of traces of flammable or toxic gases in air. In order to understand these mechanisms it is important to observe the microstructure of the sensor elements. Based on these observed microstructures, it is possible to suggest the most probable mechanisms in the detection process. It is also important to utilize other high precision instruments in determining actual composition of the samples with the view of making samples that are reproducible.

1.3 Statement of hypotheses

The following statements are presented as the major hypotheses of the study:

- The presence of Pd as impurity element in SnO_2 will reduce the temperature at which SnO_2 is operated in order to detect the presence of small quantities of CH_4 (in ppm) in air. Pd is a hydrogen-dissociating catalyst and therefore its presence on the surface of SnO_2 crystallites will lead to the dissociation of CH_4 molecules at lower temperatures compared to pure SnO_2 thus leading to an increased sensitivity to CH_4 in air at these lower temperatures. It is also expected that the temperatures at which the samples are sintered will significantly influence the sensitivity of the sensor elements to CH_4 in air.

- The amount of Pd that is added to SnO_2 in wt% would have a significant influence on its sensitivity to CH_4 in air up to a certain composition level, the optimum composition. However, above the optimum Pd composition in SnO_2, it is expected that the sensitivity to CH_4 in air will drop as a result the hindrance of the gas phase reactions on the SnO_2 semiconductor support by Pd particles. It is further hypothesized that the amount of Pd present will not influence the position of the optimum operating temperature in the detection of CH_4 in air.

1.4 Objectives of the study

- To design and construct an experimental setup for the characterization of the electrical properties of SnO_2 in gas detection.

- To determine the range of operating temperature over which SnO_2 with Pd as additive could detection CH_4 in air and identify the optimum operating temperature.

- To determine the optimum composition of Pd added to SnO_2 in the detection of CH_4 in air and to analyze the effect of sintering temperature of the samples on their sensitivity to CH_4 in air.

- To analyze the sensitivity verses concentration characteristics of SnO_2 with Pd as additive in the detection of CH_4 in air.

1.5 Thesis plan

Following the brief introduction presented in this chapter, a general review of metal oxides is given in Chapter II. This includes a review of the preparation of ceramic materials and the structure and electrical properties of these materials. Chapter III deals with the theory of gas detection using metal oxides. It begins with a review of the quantum mechanical bases of the reactivity of surface state of semiconductor materials in ambient environment. This is followed by an analysis of the theoretical bases of gas detection by metal oxides, and finally the effects of additives on the gas sensing properties of SnO_2 is discussed. Details of the sample preparation, design and construction of the experimental arrangement and the measurement techniques employed are outlined in Chapter IV. Results and discussion of the experimental work carried out on the composition, sintering and operating temperatures on sensitivity, response and recovery times of SnO_2 with Pd as additive in CH_4 detection is presented in Chapter V. The results on the relationship between sensitivity of SnO_2 and the concentration of CH_4 in air (sensitivity-concentration characteristics), cross-sensitivity studies and a comparison of the sensitivity of the sensor elements prepared in this study with those of a commercial gas sensor are given in Chapter VI. Chapter VII is devoted to the evaluation of the results on the microstructural and compositional analysis using SEM, AAS and EDAX. Finally, Chapter VIII presents the major conclusions of the research and suggestions for future studies.