CHAPTER -5

Nanocrystalline ZnO-Si Heterojunction Methane Sensor

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5.1 Introduction

ZnO presently experienced a research boom in spintronics applications as well as in SAW devices, varistors, transparent electrodes, optoelectronics and gas sensors [5.1 - 5.5]. This material contains high refractive index, high thermal conductivity, binding and UV-protection properties [5.6 - 5.8]. Such specific chemical, surface and microstructural properties of ZnO brought distinguished performance in electronics, optics, and photonics more particularly in material science application. In general, ZnO is an n-type compound semiconductor material and it has a hexagonal wurtzite structure as well as wide band gap (~3.2–3.4 eV) at room temperature [5.9]. Specific change in the procedure of its chemical synthesis is capable of largely modifying the microstructural and physical properties of ZnO. The most common forms of ZnO like rings, combs, springs, wires, belts etc. are largely accepted in the field of optoelectronics, sensors and transducers [5.10, 5.11]. ZnO received broad attention as a key technological material in gas sensor applications due to these interesting properties compared to their bulk counterpart [5.12]. Gas sensors are widely used in mines for methane detection and other monitoring activities for safety and security measures. Air quality monitoring, smoke alarms, mine and tunnel warning systems, greenhouses, LPG leak in car, in service station, storage tanks also emphasise on developing reliable, easily portable and user friendly gas sensors [5.13 - 5.15]. ZnO has a major advantage to sense at relatively much lower temperature at 150-300°C whereas other semiconducting oxides like SnO₂,
Ga2O3, Co3O4 etc., require 300–450°C to sense Methane. Such huge temperature is inconvenient for mine application [5.16]. Moreover, ZnO thin films are formed by special methods like sputtering, spray pyrolysis, CVD and sol–gel techniques [5.17-5.20]. In recent times deposition of oxide thin film by sol–gel method has attracted significant attention as it is much economically feasible and most energy saving method to deposit films of precisely controlled microstructure [5.21-5.23]. In this work a ZnO based heterojunction Methane sensor is designed. Further the characteristics of the sensor are studied by calculating the response magnitude by varying the voltage and temperature. The sensor gives ~52% response magnitude at an optimum temperature and a voltage of 250°C and 3V, respectively.

5.2 Literature survey

In the last few decades there have been tremendous advancements in the gas sensor technology [5.24-5.29]. The control of automobile exhaust emissions is an excellent example of such development. There have been sustained studies since early 1970s on oxygen sensors and have led to development of sensors for various applications with varying performance characteristics. Metal oxide based semiconductor resistive type and solid electrolyte based potentiometric, amperometric sensors are used for high temperature applications. Dissolved oxygen sensors based on Clark electrodes have played a major role for solution based pollution monitoring. Optical oxygen sensors are beginning to have an
impact for biological and medical applications in the recent times. Thus it appears that concern over environmental pollution and health issues has led to legislation over the past two decades and significant research and development efforts have been undertaken to address environmental issues. In the field of gas sensors, worldwide research has been driven by the desire to minimize emissions from various industrial sources [5.30-5.33]. In this area, oxygen sensors have played a key role in pollution control through automobile engine management, optimizing industrial boilers, cement industries, steel, biological and food processing plants and control of chemical processes [5.34]. Optical oxygen sensors have been used in the USA by many municipalities and waste water treatment plants. These optical sensors are expected to enhance their share of the package waste water market for dissolved oxygen sensors [5.35].

A group of researchers employed a nanocrystalline zinc oxide based hybrid gas sensor with signal conditioning ASIC for sensing and transmitting the information about methane concentration from the underground coal mine environment [5.36].

Several gas sensor based research works have been reported where they have used metal oxide gas sensors like tin oxide and zinc oxide for various applications ranging from domestic to environmental monitoring and industrial applications [5.37-5.40]. Alumina substrate based gas sensors of the above cited types are usually used for sensing inflammable hydrocarbon gases like methane [5.41] and other toxic gases like carbon monoxide [5.42]. But
the above cited sensors suffer from the principal limitations of relatively high operating temperature ($\geq 300^\circ\text{C}$) [5.43] and large power dissipation of around 0.5-1 watt [5.44] thereby making them not acceptable for continuous gas monitoring in several environmental situations like underground coal mines. However, there is a word of relief from agony that MEMS technology has been presently used in the field of sensor technology for miniaturization of the devices, low power consumption, faster response and greater sensitivity [5.45]. As MEMS based sensors operate at high temperature (>300$^\circ$C), a modified sensor structure has been suggested by some researchers to achieve the lower operating temperature at a relatively low cost. They have used nanocrystalline zinc oxide as the sensing material and nickel as micro heater element instead of popularly used platinum or polysilicon [5.46,5.47].

Woo-Jin Hwang et al., developed micro heaters with optimized temperature compensation design suitable for gas sensors [5.48]. They claimed that they have designed a polysilicon micro heater which is supposed to improve the uniformity of heat dissipation on the heating plate. In their power compensated design, the uniform heating area is increased by 2.5 times and the average temperature goes up by 40$^\circ$C. MEMS based sensors find wide applications as they are key components in subminiature micro sensors such as humidity sensors [5.49], wind sensors [5.50] and gas sensors [5.51-5.56]
5.3 Methodology and Result

Gas sensors exhibit improved performance by incorporation of noble metals such as Au, Pd etc. on the oxide surface\cite{5.57,5.58}. Thin film ZnO based gas sensors are widely applied for detecting explosive and toxic gases in industrial applications as well as urban and domestic life. ZnO is a polycrystalline semiconductor structure having a large number of grains and grain boundaries. The adsorption and desorption of gaseous molecules controls the electrical properties of the surface of a thin film and the surface boundaries between the grains. Oxygen ions are located at the grain boundaries. Temperature within the range of 150$^{\circ}$C-300$^{\circ}$C is required for O$_2$ to be chemically absorbed by gaining one more electron from the surface. Due to such reaction the resistivity of the material increases:

\begin{align*}
\text{O} + \text{e}^- & \leftrightarrow O^- \quad \text{[150$^{\circ}$C–300$^{\circ}$C]}, \quad (1) \\
2\text{O} + \text{e}^- & \leftrightarrow \text{O}_2^- \quad \text{[30$^{\circ}$C–150$^{\circ}$C]}. \quad (2)
\end{align*}

At the grain boundaries the Methane molecules react with the chemically absorbed oxygen resulting in negative charge carriers that are added to the bulk and hence the resistance decreases:
The oxygen atoms then go through a spillover process and at the end form negatively charged surface ions by gaining electrons from the oxide surface. This creates high electrostatic potential in the junction. The initial step is to dissociate hydrogen from CH$_4$ to produce H or CH$_3$ on the noble metal surface that reacts with adsorbed atomic oxygen to produce water. Next, the H or CH$_3$ spillover to metal oxide surface and further bonds with chemically absorbed ionic O$_2$ and produce water and free electrons that increase the current through the junction:

\[
CH_4 \rightarrow CH_3 \text{ (ads)} \ + H(ads) \quad (4)
\]

\[
CH_3^+ + H + 4O^- \rightarrow CO_2 + 2H_2O + 4e^- \quad (5)
\]

\[
CH_4 + 4O^- \rightarrow CO_2 + 2H_2O + 4e^- \text{ (Complete reaction)} \quad (6)
\]

In this particular work we have used sol-gel technique [5.22-5.24]. As per the discussed procedure 0.45M Zinc acetate dehydrate (Zn (CH$_3$COO)$_2$ • 2H$_2$O) along with Isopropanol was mixed and this mixture was stirred continuously for 1 hour at room temperature till the solution turned milky. Further Diethanolamine (DEA) was slowly added to get a clear transparent homogeneous solution. For next 24 hours aging continued and the solution was later subjected to spin coating. After that on a cleaned p-Si substrates of 4mm×4 mm dimension the prepared ZnO was spread using a spin coater. The rotation speed of the coating unit was fixed at 800 rpm while the time interval of the single coating was limited to 30seconds. Later the samples were heated at 110°C
constantly for 10 minutes. As a result the solvent melted away along with organic residuals. Lastly, the samples were annealed at 600°C to generate nanocrystalline ZnO. This complete method was repeated for three consecutive times and a ZnO film of 900 nm thickness with the particle size ranging from 45nm to 75 nm was produced.

5.4 Structural Analysis

Figure 5.1(a) is a schematic of the heterojunction sensor structure with one ZnO side Au and silicon side Al contact. The metallic contacts were formed by depositing Au and Al using Al metal masks by e-beam evaporation technique at a base pressure of 10–6 mbar. The contact area was 2 mm X 2 mm.
SEM Analysis

Figure 5.1(b) depicts the SEM micrograph of ZnO film deposited by sol-gel technique. Multiple deposition steps have been used to achieve this specific three layer thin films of ZnO. Although decrease in the number of coating applications considerably reduces both drying steps required and also the number of interfaces within the resultant thin film which can contribute to reduced optical transparency.

![Figure 5.1(b) SEM Analysis for Sample](image)

5.5 I–V Characteristics and sensor studies

The sensor related experimental reading was taken in a closed (10 cm X 4 cm) ‘U’ type glass tube. This glass tube consisted of inlet and outlet for gases and it was placed coaxially on a resistively heated furnace having a 4cm constant temperature zone. The temperature was limited to ± 1°C by means of a copper constantan thermocouple which is in-built in the precise temperature controller. To make perfect electrical connections, fine copper wire and silver paste was used as it is the best alternative for creating metallization contacts. To study the
sensing characteristics, Methane gas of high purity (100%) and IOLAR grade N2 in appropriate proportions were allowed to flow to the gas-sensing chamber through a mixing path via Alicat Scientific Mass Flow Controller & the mass flow meter respectively. The mass flow rate as well as the relative concentrations of the gases was set to constant during the entire experiment. The gas pressure on the sensor device was 1 atmosphere throughout the experiment. The current–voltage characteristics of the sensors first in presence of Methane gas and then in the absence of Methane gas were calculated using a precise Agilant Multi-meter and voltage source. Figures 5.2(a) and 5.2(b) reveal the forward bias I–V characteristics of ZnO–Si heterojunctions with Au and Al contacts to ZnO, correspondingly in the temperature range of 50–250°C and exhibited the rectifying nature in both the cases.

5.6 Calculation of Response magnitude

The sensitivity to 1% Methane concentration was traced in a wide operating temperature range from the very beginning of the measurement process to obtain the optimum temperature for highest sensitivity. The response magnitude(RM), of a specific voltage, is correlated to forward bias sensor current in air denoted by (Ia) and in test gas (Ig) using an equation

\[ RM = \frac{(Ig - Ia)}{Ia} \times 100 \]  

(7)

5.7 Results and Discussions

Due to exposure of target gas, the sensor current increases rapidly with time and soon it obtains a stable value. This particular range of sensor current,
denotes the completion of sensing process, and is defined as the equilibrium current value. This specific value of equilibrium resistance is used to calculate the percentage of sensitivity. The percentage sensitivity is further described as saturation sensitivity. As per the V-I characteristics shown in Fig. 5.2 (a) and 5.2(b) the response magnitude of the designed device was calculated using equation (1). The same has been shown in the Fig.5.3(a) and 5.3(b) respectively. From the figure it is clear that the optimum voltage and the temperature of the device are 3V and 250°C respectively. In this particular Voltage and Current the sensor gives us maximum response which is denoted as Response Magnitude. Increase in temperature beyond 250°C the response of the sensor reduces upon the exposure of the target gas.

Figure 5.2(a) V-I characteristics with gas
Figure 5.2(b) V-I characteristics without gas

Figure 5.3(a) Response magnitude vs. Voltage
Figure 5.3(b) Response magnitude vs. Temperature
References

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