Chapter 6

Summary and Conclusion

6.1 Introduction

This chapter outlines the summary and major conclusions pertaining to the present work. The basic purpose of the present work is to explore the comprehensive investigation of developed nanoparticles based ZnO-resistor and Pd/ZnO Schottky diode upon exposure of NO_2 and H_2 gas. The present study has reported a sol-gel chemical method for the synthesis of ZnO nanoparticles and further, it has been characterized by various techniques such as XRD, EDS, FE-SEM, and AFM. The detailed study of nanoparticles reveals the hexagonal wurtzite phase of ZnO having a size in the range of ~ 25 to ~ 110 nm.

The resistive sensor has been fabricated using brush-coated ZnO nanoparticles and its NO_2 sensing mechanism has been described in form of physisorption and chemisorptions of exposed NO_2 molecules upon the ZnO surface. On the other side, the facile Pd/ZnO Schottky diode has been fabricated on a glass substrate in order to replace the silicon substrate which includes the conventional tedious fabrication process such as RCA Cleaning, photolithography and oxide growth etc. The gas sensing mechanism of Pd/ZnO Schottky diode has also been explained with the help of an energy band diagram. The present thesis comprises six chapters including chapter on conclusion and future scope.

6.2 Summary and Conclusion

Chapter 1 discusses the two critically environmental gases H_2 and NO_2 along with their detection techniques such as electrochemical, infrared, ultrasonic, thermal and solid-state based gas sensors. Among all these sensors, the solid-state sensor is a prominent one because of its wide spectrum of gas detection and easily producible. The various solid-state gas sensors (such as a chemi-resistor, MOS Capacitor, Metal-semiconductor Schottky diode, and field effect transistor) have been briefly discussed.

In this chapter, the literature survey has shown ample opportunities to improve the gas sensing performance. The chapter analyzes the various resistive and Schottky based gas sensors; reported by the learned researchers and scientist. They have explored a variety of resistive gas sensors, based on ZnO, SnO_2, WO_3 and TiO_2 material. These sensors exhibit 2 or 3-dimension nano-architecture, highly porous and chemically treated structure. In addition to the resistive sensor, the chapter has also covered the literature review on Schottky diode based gas sensors. In a Schottky type sensor, the sensing layer is sandwiched between Schottky and Ohmic contact materials. The researchers have reported different kinds of Schottky structures such as pseudo, super-lattice, ultra thin insulating sandwich etc. in order to improve the gas sensing performance even at room temperature. As per the available inference of the literature, it has been observed that the nanostructures improve the sensitivity of sensor upon exposure to different oxidizing and reducing gases such as CO, H_2, NO_2 CO_2, NH_3 etc due to its unique large surface to volume ratio. The emergence of nano-structures has brought revolution in the field of gas sensor and it could be exploited with engineered approach in order to enhance sensors performance. These nanostructures motivate the development of such a gas-sensor that meets all the essential and logical requirement of the sensor. Based on the literature survey, the problems of thesis work are listed below:

- To simplify the exhaustive paste preparation method in thick film gas sensors i.e. preparation of glass powder and vigorous mixing of organic binder etc.

- To simplify the exhaustive fabrication process in thin film gas sensors i.e. oxide growth, photolithography and RCA cleaning etc.
- To fabricate selective and reproducible sensor
- To improve the sensitivity of the sensor particularity at low-temperature range.
- To minimize the fabrication cost.

The chapter has also justified the author's discretion of framing objectives of nanoparticles based resistor and Schottky diode as gas sensors. The organization of the present thesis has been outlined in the last section of this chapter.

Chapter 2 discusses about the micro-gas sensors and gas sensing materials. The performance parameters of the micro-gas sensors have been elaborated by the sensitivity, selectivity, stability, response and recovery time. This chapter has also categorized the gas sensing materials into four subcategories (i) semiconducting Metal oxide (SMO) (ii) polymers and (iii) transition metal dichalcogenide and (iv) carbon allotropes etc. Among all these, SMO based material (such as ZnO, SnO_2, TiO_2 etc.) is a promising candidate because of its long-lasting, reproducible and stable gas sensing response. Nowadays, ZnO has gained popularity among several SMO materials because of its high thermally stable response. ZnO is an n-type piezoelectric material having wide bandgap (3.37 eV) and a large exciton binding energy (60 meV). The gas sensing properties of ZnO material has also been discussed with the help of two sorption methods: physisorption and chemisorption.

Chapter 3 presents the sol-gel chemical method for the synthesis of ZnO nanoparticles and fabrication of brush coated ZnO-resistor. This chapter also describes the facility available for thick film technology based device fabrication and characterization such as manual thick film printer, oven, conveyor belt furnace and self-developed measurement set-up. In addition to that, this chapter has also briefed on material characterization tools such as SEM, XRD, AFM, and EDS. The major observations of this chapter are given below:

- ✓ EDS confirm the presence of Zn and O element in the nanomaterials
- ✓ FE-SEM, confirms the particles size in the range of ~ 25 to ~ 110 nm
- ✓ AFM reveals the roughness of film ~ 136.303 nm.
- ✓ XRD reveals the polycrystalline hexagonal wurtzite structure of zinc oxide.
- ✓ The brush coated ZnO-resistor has been tested under various gases such as NO_2, H_2, CO, ethanol, and propanol in the temperature range from 150 to 350 °C.
- ✓ Among all these exposed gases, NO_2 has reported highest sensitivity ~ 945 %/ ppt at operating temperature 280 °C.
- ✓ The obtained results have been explained by the surface and subsurface adsorption of NO_2 molecules at available trap sites (oxygen ions) on the nanoparticles (ZnO) surface.
- ✓ The increased NO_2 concentration has affected the response and recovery times; the response time decreases from ~ 4 to ~ 2 s with an increase in recovery time from ~ 5 to ~ 20 s.
- ✓ In comparison with others reported sensor, the brush-coated ZnO nanoparticles based NO_2 sensor exhibits a very facile device which shows a very fast response and recovery time.

Chapter 4 reports a facile fabrication of Pd/ZnO nanoparticles based Schottky diode on a glass substrate. This chapter also presents the available facilities being used under the thin film technology based device fabrication and characterization such as a Spin coater, bench furnace, thermo-chuk, semiconductor parameter analyzer and a manual ellipsometer. The obtained observations of this chapter have been summarized as below:

- ✓ XRD reveals the hexagonal wurtzite phase of ZnO film
- ✓ FE-SEM depicts the nanoparticles size in the range from ~ 25 to 110 nm.
- ✓ AFM depicts the roughness of the film around ~ 52.73 nm.
- ✓ Developed Pd/ZnO nano-particles based Schottky sensor has been characterized in the voltage range from - 1 to 1 V upon exposure of NO_2 concentration ranging from 10 to 50 ppm.
- ✓ The sensitivity of the sensor has been observed from ~ 16 to ~ 45.2 % with excellent repeatability.
- ✓ The possible reason for the high sensitivity is believed to be the creation of an interfacial dipole layer at Pd/ZnO interface due to the presence of an oxygen trap site at Pd/ZnO interface.
- ✓ These interface dipole moments provide an additional increase in the barrier height from ~ 0.675 eV to ~ 0.727 eV and ideality factor from ~ 3.175 to ~ 5.608 both.
- ✓ This fabricated Pd/ZnO sensor has shown a fast response time (~ 45 s) and recovery time (~ 250 s), which are important consideration for any sensing device.
- ✓ This fabricated sensor is not only cost-effective but also highly sensitive for NO_2 detection at room temperature.
- ✓ These appealing features of the device make an attractive sensor capable of NO_2 detection at low concentration.

Chapter 5 has investigated the hydrogen sensing characteristic of developed Pd/ZnO nanoparticles based sensor. Key observations of this chapter have been summarised below:

- ✓ The sensor's performance paramerters (sensitivity, repeativity, response and recovery time) has been investigated in the temperature range from 75 to 110 °C. The optimized result has been observed at a temperature of 90 °C.
- ✓ The optimized sensor at temperature of 90 °C shows the maximum sensitivity of ~ 246.22 % with minimum response and recovery time of 53 and 265 s respectively at 2000 ppm H_2 conc. with excellent repeatability.
- ✓ The change in barrier height and ideality factor of diode has also been evaluated in terms of change in the I-V characteristic upon exposure to hydrogen gas in the concentration range of 200-2000 ppm. Both diode parameters follow the same decreasing trend with increase in H_2 concentration.
- ✓ The sensing mechanism described by the conventional Pd surface adsorption and subsequently dissociation of H_2 gas and diffusion into Pd catalyst. Further, these diffused atoms chemisorbed on available trap sites at Pd/ZnO interface and form dipole moments and results in decrease in barrier height and ideality factor of the device.
- ✓ A qualitative energy band diagram has been presented to clarify the creation of dipole layer at the Pd/ZnO interface in presence of H_2 gas.
- ✓ The developed Pd/ ZnO based sensor has been found not only cost-effective and high sensitive towards H_2 gas but also possesses a reproducible response.

6.3 Future Scope of Work

Research is a never-ending continuous process; there are ample opportunities to derive future scopes of research from the present work. Some of them are listed below:

- Synthesis of *doped*-ZnO nanoparticles using some doping elements such as Sodium (Na), Potassium (K), Palladium (Pd), Gold (Au), Aluminium (Al) etc and ZnO-

composite using other semiconducting metal oxide materials such as ZnO-SnO_2, ZnO-TiO_2, ZnO-WO_3 etc.

- The Pd metal in Pd/ZnO Schottky contact can be replaced with other transition materials such as Au, Pt, and Ag etc. in order to understand their effects on gas sensing performance using various metal contacts.
- In the present scenario, the soda lime glass substrate of Schottky diode can also be replaced with flexible SCHOTT ultra-thin glass as shown in Figure 6.1 (a).
- The gas response can be observed with various gases (H_2, NO_2, ethanol, propanol etc) in the presence of ultraviolet radiation as shown in Figure 6.1 (b).

(a) **(b)**

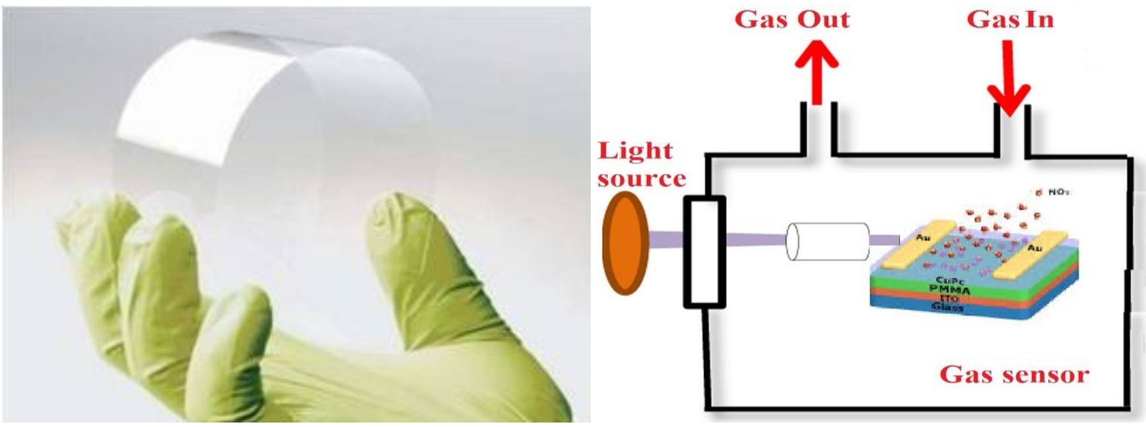

Figure 6.1: The prospective work can be done (a) using SCHOTT flexible substrate [IR 5] (b) under the presence of UV radiation.

Reference

[IR 5] http://www.globalsources.com/manufacturers/Flexible-Glass.html.