Chapter 5

Hydrogen Sensing using Pd/ZnO Nanoparticles based Schottky Diode at Low Temperature

5.1 Introduction

Nowadays, hydrogen is being used as a clean energy source, metal smelting, glassmaking, semiconductor processing, petroleum extraction and in the daily chemical industry etc. because of its strong reducing behavior (Gu, Wang and Hu, 2012). Hydrogen is flammable, odorless, colorless, tasteless and explosive (at 4 % hydrogen in air) (Tsai *et al.*, 2008) gas and can't be detected by human senses (Webster, John G., 2014). Therefore monitoring and detection of H_2 detection are very useful for preventing to the risk of explosion and fire. Solid state H_2 sensor based on semiconductor metal oxide such as SnO_2 (Choi *et al.*, 2014; Van Toan *et al.*, 2016), ZnO, TiO_2 (Hazra *et al.*, 2013) are currently being investigated as gas sensing materials. Among these sensing materials, ZnO is being widely used for H_2 sensor because of its non-toxicity, good electrical, optical, piezoelectric, chemical and thermal stability at a low price. However, a high operating temperature is generally required for the better performance of ZnO based H_2 sensors. Further enhancement in the sensor's sensitivity can be done by surface modification, catalytic doping, and nanostructure. These techniques prevail for good gas sensing response at relatively lower temperature. The nanostructure of the ZnO thin film leads to numerous adsorption site and high surface to volume ratio which increases the interaction of gas molecules to the sensor's surface, which results increase in the sensitivity of the sensor.

Several hydrogen sensors have been discussed in the literature review reported by learned scholars for improving hydrogen sensitivity using various technologies and structures. But, it is still a challenging task to achieve appreciable low concentration H_2 sensitivity at low operating temperature with cost effectiveness. Therefore, the present work has made an effort for achieving a high H_2 response at relatively low operating temperature using ZnO nanoparticles based Schottky diode. In this chapter, the fabricated Pd/ZnO nanoparticles based Schottky diode is being used for hydrogen sensing at a relatively low temperature. The obtained results have been explained through surface and subsurface adsorption of a hydrogen atom on the Pd surface; subsequently, its diffusion to ZnO nanoparticles surface where these hydrogen atoms are trapped in the available traps sites (oxygen ions). These trapped hydrogen atoms give rise to the formation of dipole moments, resulting in the decrease in barrier height. The resulting decrease in barrier height increases the current of the Schottky diode which manifest itself in the form of increase in sensitivity of the sensor.

5.2 Experimental details

This section discusses the fabrication and structural properties of Pd/ZnO nanoparticles based Schottky diode. The measurement step-up for hydrogen detection has also been covered in the section.

5.2.1 Device Fabrication and structural properties

The fabrication of Pd/ZnO nanoparticles based Schottky diode on aluminum coated glass substrate has already been discussed in the chapter 4. The film structural properties have also been characterized by the FE-SEM, AFM, XRD, and EDS.

5.2.2 Measurement set-up for hydrogen detection

H_2 detection using the developed Pd/ZnO sensor has been carried out in the experimental set-up as shown in Figure 5.1. The set-up consists of an airtight stainless steel test chamber of 10, 000 cc volumes with the provision of gas inlet-outlet ports and gas injected through rubber lid provided of the plate of test chamber. The sensor has been characterized by keeping the SUT (sensor under test) in the test chamber and connected to the parameter analyzer (Keysight B1500A). Parameter analyzer measures the I-V characteristics of SUT upon exposure of H_2 gas (purity 99.99 %, purchased by Sigma-Aldrich) injected into the test chamber through an air tight syringe. The hydrogen concentration in the test chamber is change from 200 to 2000 ppm and the I-V characteristics have been simultaneously recorded. Afterward, the SUT was exposed to air by opening the outlet valve of the test chamber for recovery of sensor. The H_2 concentration is calculated by the Equation (5.1).

$$H_2 \text{ Concentration (ppm)} = \frac{H_2 \text{ Concentration (Litre)}}{\text{Closed Chamber Volume (Litre)}} \quad (5.1)$$

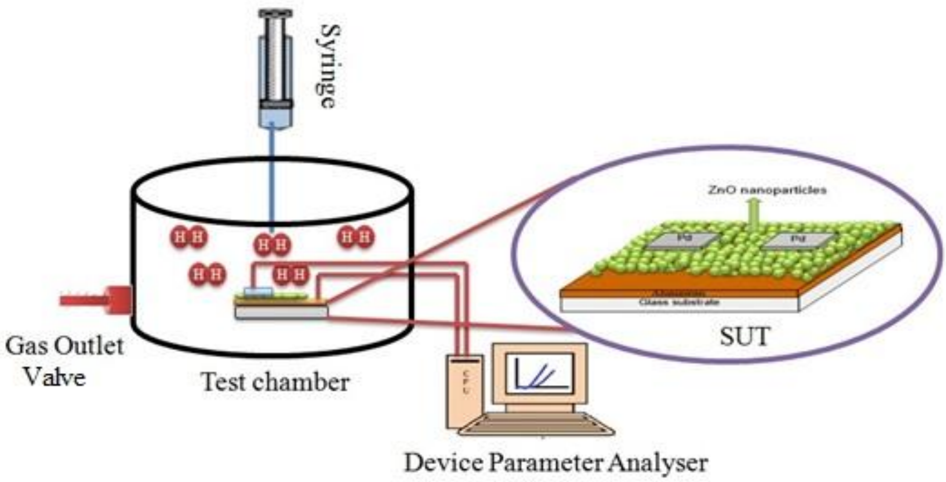


Figure 5.1: Schematic of H_2 measurement set-up.

5.3 Results and discussions

This section discusses the temperature and hydrogen gas effect on the fabricated Pd/ZnO nanoparticles based Schottky sensor.

5.3.1 Temperature effect on Pd/ZnO Schottky diode

Semiconductor device parameter analyzer (keysight B1500A) has been used to observe the effect of temperature on the I-V characteristic of Pd/ZnO diode in the temperature range of 25- 110 °C as shown in Figure 5.2 (a). It is found that the tremendous decrease in the diode current at a fixed bias of 1V an increase in temperature as shown in Figure 5.2 (b). This drastic decrease in current might be occurring due to the domination of lattice scattering (Morin, 1954; Dr. S. Parasuraman, 2014) in Pd/ZnO diode. Lattice scattering is a dominant phenomenon of semiconductor at a surplus temperature which drastically reduces the carrier mobility as temperature increase that results decrease in diode current.

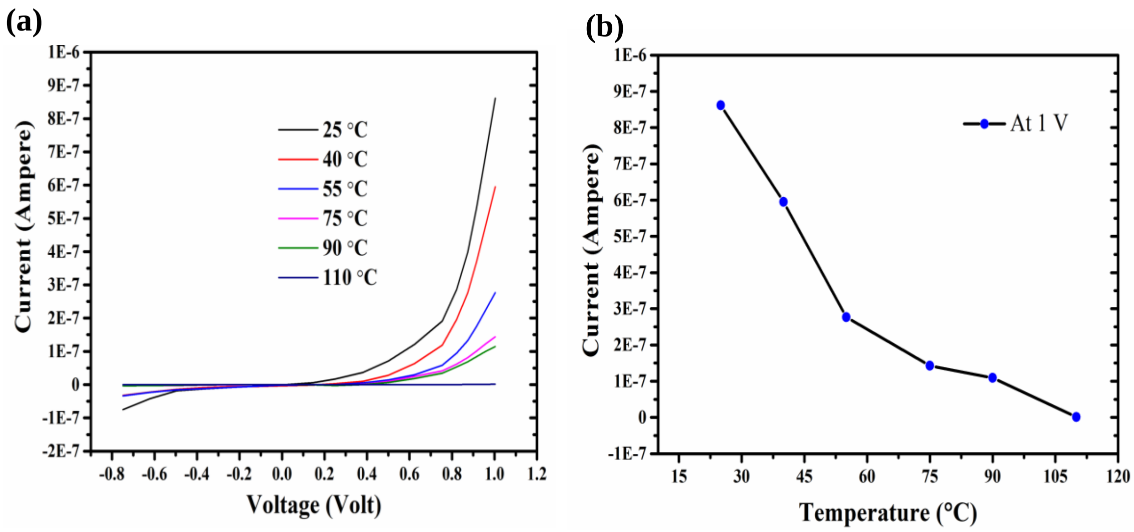


Figure 5.2: (a) I-V characteristics and (b) diode forward current of Pd/ZnO Schottky diode due to change in the temperature range from 75 to 110 °C.

5.3.2 Hydrogen Sensing Results

The sensing properties of Pd/ZnO sensor upon H_2 exposure has been investigated by the I-V characteristic of Pd/ZnO nanoparticles based Schottky diode. Figure 5.3 (a), (b) and (c) show the forward and reverse biased I-V characteristics of Pd/ZnO Schottky diode upon exposure of various H_2 concentrations ranging from 200 to 2000 ppm at temperature 75, 90 and 110 °C respectively. The inset of Figure 5.3 (a), (b) and (c) represents the logarithmic plot of the I-V characteristic. The forward I-V characteristic of the Schottky junction can be described by thermionic emission model that imply the forward current (I) by Equation (5.2) (Aydoğan *et al.*, 2009)

$$I = I_0 \left[\exp\left(\frac{qV}{\eta kT}\right) - 1\right] \quad (5.2)$$

Where η is ideality factor, k is Boltzmann constant 1.38 x 10^{-23} J/K, T is operating temperature in Kelvin, V is applied forward bias voltage, q is electronic charge and I_0 is the reverse saturation current of Pd/ZnO Schottky diode. I_0 is calculated using ln (I) vs V plot in low bias (0 to 0.5 V) by a linear interception at zero volt (Chiu *et al.*, 2009). The other dependent parameter is the ideality factor (η) which can be easily calculated by the Equation (5.3), (Chiu *et al.*, 2009) shown below.

$$\eta = \left\{\frac{q}{kT}\right\} \times \left\{\frac{\partial V}{\partial \ln(I)}\right\} \quad (5.3)$$

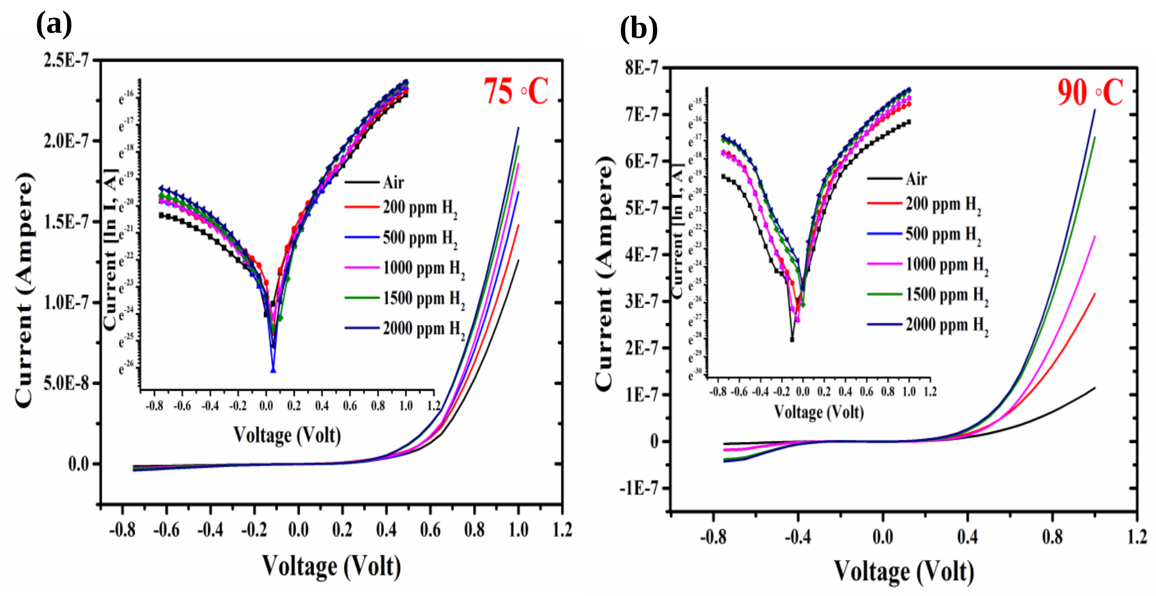
Where, η is extracted from the slope of the linear region of ln (I) vs V plot at low bias (0 – 0.5 V). The most important parameter of Schottky diode is barrier height (Φ_B) or Schottky barrier height which can be calculated through the relation given in Equation (5.4) (Huang *et al.*, 2011).

$$q\emptyset_B = kT \ln\left(\frac{AA^{**}T^2}{I_0}\right) \quad (5.4)$$

Where A is the effective contact area of diode 15 mm^2, A** is effective Richardson constant 32 $A\text{-}cm^{-2}\ K^{-2}$ (Al-Ghamdi, Al-Heniti and Mahmoud, 2013; Kaphle and Hari, 2016) which is the standard value for ZnO. Table 5.1 shows the change in barrier height (Φ_B), ideality factor (η) and reverse saturation current (I_0) as a change in H_2 concentration ranging from 200 to 2000 ppm at temperature 75, 90 and 110 °C. Figure 5.3 (d), (e) and (f) depict the decrease in barrier height (Φ_B) and ideality factor at temperature 75, 90 and 110 °C respectively.

Table 5.1: Change in diode parameters with H_2 concentration and operating temperature.

H_2 Conc. ppm	75 °C			90 °C			110 °C		
	Φ_B (eV)	η	I_0 (pA)	Φ_B (eV)	η	I_0 (pA)	Φ_B (eV)	η	I_0 (pA)
0	1.125	2.59	0.29	1.204	2.52	0.12	1.290	2.49	0.07
200	1.122	2.51	0.33	1.193	2.24	0.17	1.266	2.28	0.15
500	1.120	2.45	0.35	1.189	2.08	0.19	1.264	2.24	0.16
1000	1.117	2.40	0.38	1.188	1.99	0.20	1.260	2.19	0.18
1500	1.116	2.36	0.39	1.187	1.93	0.21	1.257	2.15	0.19
2000	1.115	2.32	0.40	1.186	1.90	0.22	1.255	2.13	0.21



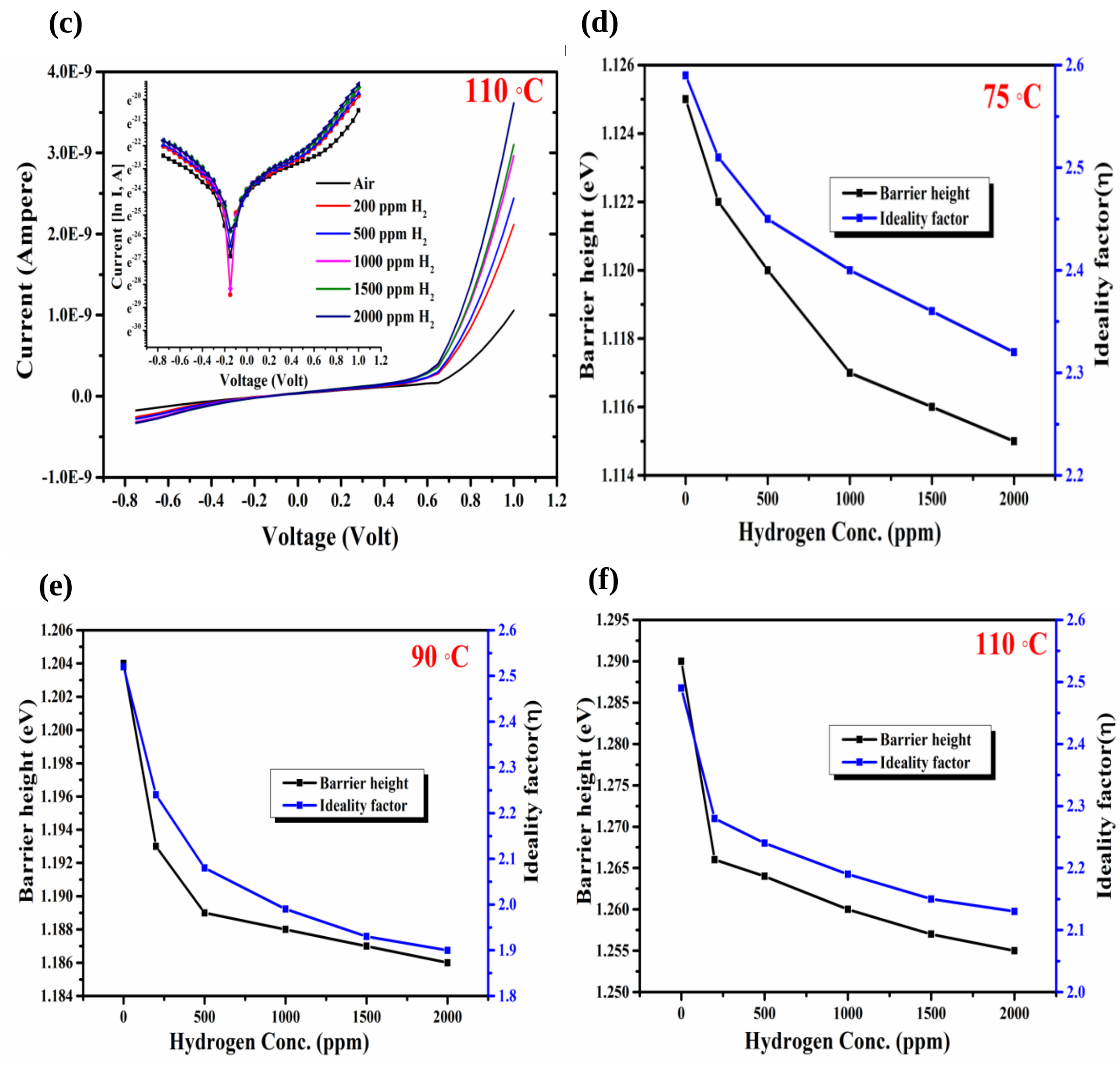


Figure 5.3: I-V characteristics of Pd/ZnO diode at (a) 75 °C (b) 90 °C and (c) 110 °C where inset shows the ln (I) vs V plot. Change in ideality factor and barrier height upon exposure to H_2 concentration ranging from 200 to 2000 ppm at (d) 75 °C (e) 90 °C (f) 110 °C.

The change in current of Pd/ZnO sensor upon exposure of H_2 gas can be explained as follows: when Pd/ZnO sensor exposed to the air, the environmental oxygen adsorbs to the Pd surface and then diffuse to the ZnO surface (Basu *et al.*, 2008; Das *et al.*, 2010). These oxygen atoms are chemisorbed to ZnO surface and form oxygen ions which act as a trapped sites for hydrogen atoms. The nanostructure of the ZnO enhances the trap site of the surface due to large surface to volume ratio. On the other hand, when H_2 expose upon Pd/ZnO sensor, it is adsorbed to the surface and subsurface adsorption site of Pd metal (Chiang *et al.*, 2010) and dissociates into hydrogen atoms (H+H) (Ekedahl and Lundstro, 1998), (Litovchenko *et al.*, 2004). These hydrogen atoms further diffuse into Pd on Pd/ZnO interface in addition to spillover phenomenon has also been reported. At the interface, these hydrogen atoms are trapped by the already existing oxygen ions and they form dipole moments at the interface which decreases the barrier height of the Pd/ZnO Schottky diode as shown in Figure 5.4. These dipole moments led to an increase in width of the depletion region at the Pd/ZnO interface which causes a decrease in the barrier height and ideality factor of the Schottky diode.

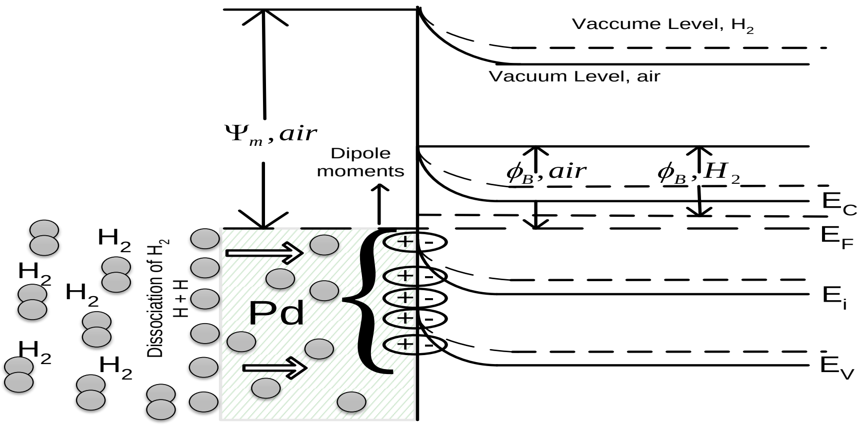


Figure 5.4: Energy band diagram representation for change in barrier height due to H_2 gas molecules.

The change in barrier height ($\Delta\ \Phi_B = \Phi_{B,air} - \Phi_{B,H2}$) occurring may be mathematically defined by Equation (5.5) (Chiu *et al.*, 2009; Bishop *et al.*, 2015)

$$\Delta\ \Phi_B = \frac{\mu N_i \theta_i}{\varepsilon_s} \tag{5.5}$$

Where μ is effective dipole moments, N_i is the number of total sites per area at the interface, ε_s is permittivity of the surface, θ_i is the coverage of trap sites at the interface. Furthermore, when the exposed gas is removed from the test chamber by opening the outlet then the diffused atom starts leaving the Pd surface slowly but not completely. This ejected atom reduces the dipole moment and results in decrease in width depletion region at the interface which in turn increases the barrier height to original value as in the air. I –V characteristic of Pd/ZnO sensor was studied at different temperatures in the range 75 – 110 °C. The magnitude of sensitivity was evaluated using the Equation (5.6) (Huang *et al.*, 2011).

$$S\ (\%) = \frac{I_{H_2} - I_{air}}{I_{air}} \times 100 \qquad (5.6)$$

Where, I_{H_2} is diode current in H_2 and I_{air} is diode current in air.

The transient response at operating temperature 75, 90 and 110°C against H_2 concentration 200, 500, 1000, 1500 and 2000 ppm have been investigated as shown in Figure 5.5 (a), (b) and (c). Initially, all transient responses reveal a linear increase in sensitivity till 1000 ppm H_2; due to a linear increase in H_2 concentration lead to a linear increase in the formation of dipole moments, as a result, linear increase in the sensitivity. Furthermore, sensitivity shows a saturation trend in the range 1000 to 2000 ppm H_2 Conc. The most probable reason of saturating trends is the complete filling of all the available trap sites at Pd/ZnO interface. Figure 5.5 (d) represents the sensitivity Vs temperature (ranging from 75 – 110 °C) plot of the sensor with varying H_2 concentration from 200 – 2000 ppm. The optimized response has been observed at temperature of 90 °C. In Figure 5.5 (d) the sensitivity increase linearly from 75 to 90 °C; most probably due to large diffusion of environmental oxygen into Pd metal to ZnO surface which increases the trap sites (oxygen ions on ZnO surface). This result enhances the dipole moments at the Pd/ZnO interface that lead to increase in the sensitivity value. Further, due to increase in temperature, the sensitivity drops indicating the reduction in dipole moments at Pd/ZnO interface due to a decrease in trap sites caused by desorption of oxygen ions from the Pd/ZnO interface (Basu *et al.*, 2008; Van Toan *et al.*, 2016). The interesting low-temperature hydrogen (H_2) gas sensing implies the crucial role of Pd metal (catalytic) (Ekedahl and Lundstro, 1998; Litovchenko *et al.*, 2004; Chiang *et al.*, 2010) which adsorbs the H_2 gas at low temperature and dissociates into hydrogen atoms (H + H). The Pd catalyst aids these hydrogen atoms to diffuse to Pd/ZnO interface to form dipole moments.

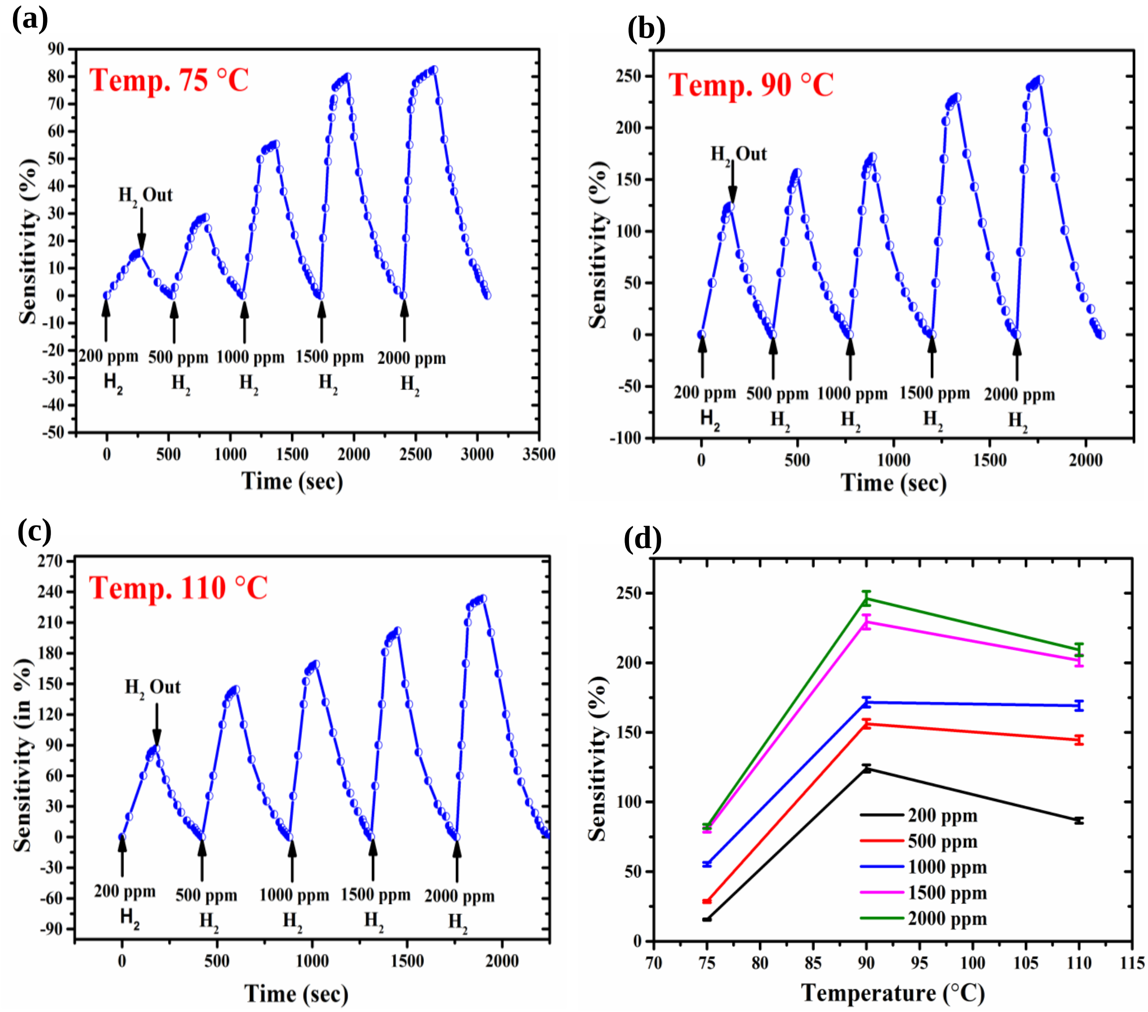


Figure 5.5: Transient response at (a) 75 °C, (b) 95 °C, (c) 110 °C and (d) Sensitivity Vs temperature plot of Pd/ZnO sensor under-exposure of 200 – 2000 ppm H_2 concentration.

The response time of Pd/ZnO sensor is calculated using time taken by the sensor to reach 90% of its peak sensitivity value (Thu *et al.*, 2017) and similarly recovery time is measured by the sensor to reach back to 90% of its original value (before exposure of gas) (Kadhim, Abu Hassan and Abdullah, 2016; Thu *et al.*, 2017). Both response and recovery time are a function of operating temperature as well as H_2 concentration (Neri *et al.*, 2007; Wang and Shaikh, 2015; Van Toan *et al.*, 2016) as shown in Figure 5.6 (a) and (b). Figure 5.6 (a) shows the decreasing trend in response time in the temperature range from 75 to 90 °C. This response time reduction is due to the very fast formation of dipole moments at Pd/ZnO interface by enhancing the rate of adsorption and absorption of H_2 gas (Van Toan *et al.*, 2016). Furthermore, increase in the temperature range from 90 to 110 °C, the rate of absorption of hydrogen atom decrease (Neri *et al.*, 2007) and also reduces the dipole moment at the interface of Pd/ZnO which leads to increase in the response time. Figure 5.6 (b) represents recovery time which implies the time taken by the hydrogen atom for completely desorbing (Neri *et al.*, 2007) from the Pd catalyst during recovery of the sensor. But practically it is not possible to desorb out all trapped hydrogen atoms in the Pd catalyst. The recovery time has shown the same temperature dependency as that of the response time. Temperature range from 75 to 90 °C shows the very fast desorbing rate of the trapped H_2 atom which represents a decreasing trend of recovery time. The recovery time of the sensor was found minimum at a temperature of 90 °C and beyond this temperature, the rate of desorbing of trapped hydrogen atom slow down which led to an increase in the recovery time. Table 5.2 shows the approximate sensitivity (S), response time (τ_R) and recovery time (τ_C) at a various operating temperature and hydrogen concentration.

Table 5.2: Sensor's parameters at different temperature ranging from 75 to 110 °C.

H_2 Conc.	75 °C			90 °C			110 °C		
Ppm	S (%)	τ_R sec	τ_C sec	S (%)	τ_R sec	τ_C sec	S (%)	τ_R sec	τ_C sec
200	15.61	209	214	124.1	123	186	86.66	144	201
500	28.57	184	251	156.2	99	223	144.5	127	228
1000	55.26	141	286	171.6	84	241	169.2	87	246
1500	79.84	109	339	219.3	71	252	186.6	73	254
2000	82.45	86	353	246.2	53	265	233.3	59	272

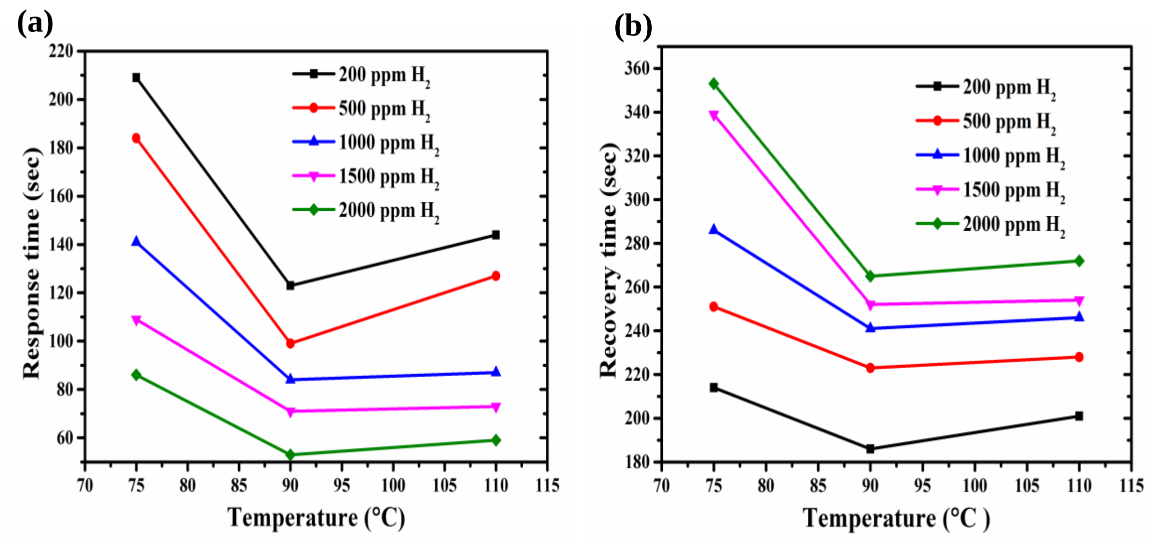


Figure 5.6: Effect of temperature on (a) Response time and (b) Recovery time for 200 to 2000 ppm H_2 gas concentration in the temperature range from 75 to 110 °C.

The repeatability of Pd/ZnO sensor is also a very important parameter of any sensors which reveals the reliability of the sensor. Figure 5.7 shows the three consecutive sensor sensitivity under repetitive 500 ppm H_2 exposure at 90 °C which reveals the ~ 144.54%, ~ 146.21% and ~ 141.46% H_2 sensitivity. It is observed that the sensitivity of the sensor is reproducible as possess a similar response.

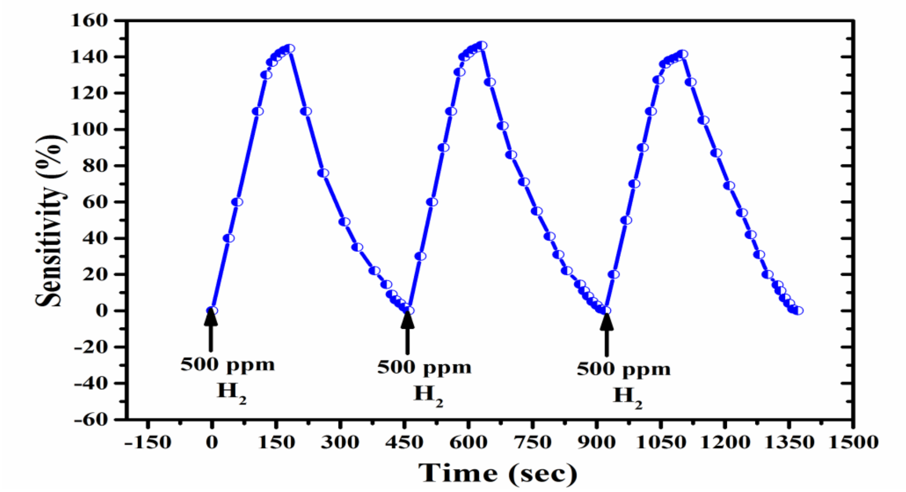


Figure 5.7: The repeatable transient response of Pd/ZnO sensor upon repeatable exposure of 500 ppm hydrogen gas at 90 °C.

5.4 Conclusion

The nanostructure of the ZnO thin film led to numerous adsorption site, large trap sites and high surface to volume ratio etc. The Pd/ZnO Schottky diode has been developed in previous chapter 4. The present chapter has investigated the H_2 gas (200 to 2000 ppm) sensitivity of Pd/ZnO Schottky sensor in the temperature range from 75 to 110 °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 excellence repeatability.

The Pd/ZnO Schottky diode parameters such as barrier height and ideality factor have also been evaluated upon exposure to 200 – 2000 ppm concentration of H_2 gas. The H_2 sensing mechanism has been described by the conventional Pd surface adsorption 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. 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. It results in a decrease in barrier height and ideality factor of the Schottky diode. Pd/ZnO NPs based sensor is not only cost-effective and highly sensitive but also possesses a reproducible response along with high response and recovery time.

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