6

Schottky-Contacted Vertically Self-Aligned ZnO Nanorods for Hydrogen Gas Nano-Sensor

In this chapter, the effect of Schottky contact between metal and self-aligned ZnO NRs on senor's response and response/recovery time are discussed. Initially, nanosensor fabrication and optimization have been performed. Structural, optical and surface morphology of ZnO NRs were studied to confirm crystallinity and uniform distributed deposition of ZnO NRs on n-Si substrate. Furthermore, resistance responses of Au Schottky contacted nanosensors were observed in the range of 50 to 150 °C with 1% and 5 % hydrogen concentration in argon environment, which is below and above the explosive limit (4%) of hydrogen in air. For both hydrogen concentrations, response/recovery time is also evaluated. Then, a sensing mechanism is proposed based on Schottky barrier height changes at heterojunctions. In progression to sensor's relative response, Pd Schottky contacted ZnO NRs based hydrogen sensors achieved ppm level hydrogen detection from 5ppm to 10,000 ppm (1%) for operating temperature ranging from 50 °C to 175 °C, respectively. These nanosensors also displayed high relative response for small hydrogen concentration with fast response/recovery time. These sensors selectivity also discussed in presence of various gases.

6.1 INTRODUCTION

In preceding chapters, we have discussed about ZnO nanorods based hydrogen sensor. Gas sensor response & selectivity can be modified by changing properties like metal oxide crystallinity, catalyst doping, metal contact variation and operating temperature [Gu *et al.*, 2012; Bochenkov and Sergeev, 2010; Sathananthan *et al.*, 2009]. By varying operating temperature and hydrogen concentration level, gas sensor's response/sensitivity, response/recovery time can be varied to large extent [Bie *at al.*, 2007; Hung *et al.*, 2009; Park *et al.*, 2010]. For further enhancement of gas sensor's response and response/recovery time, Schottky barrier height in presence of reactive gases can be adjusted [Zhou *et al.*, 2009]. Schottky barrier height can be highly amended by adsorption/desorption of oxygen which in return, will radically increase sensor's sensitivity [Al-Zaidi *et al.*, 2011]. Due to change in barrier height, electron concentration varies at junction which in turn, changes resistivity of nano sensors [Yu *et al.*, 2010; Shafiei *et al.*, 2010; Zhang *et al.*, 2008]. At high temperature, relative change in resistivity is enormous in comparison to low operating temperature as surface adsorption/desorption of gases enhances with increase in temperature. Das *et al.* in [Das *et al.*, 2010] fabricated Pt/ZnO single nanowire Schottky diode using e-beam lithography that gave 90 % sensitivity at room temperature with fast response time of about ~55 sec. Pandis *et al.* in [Pandis *et al.*, 2007] found that Au nanocrystals with ZnO improved the sensing response and reduced operating temperature up to 150 °C. Wei *et al.* in [Wei *et al.*, 2009] also described that the presence of Schottky barrier in addition to ohmic contact enhanced surface chemisorbed reactions and showed 4-time higher sensitivity than ohmic junction.

6.2 EXPERIMENTAL SETUP

Initially, ZnO nanorods were deposited on *n*- type Si (100) substrate using RF magnetron sputtering System. Chemical cleaning process was performed for eliminating native oxide layer and other contaminations from silicon substrate followed by 5% HF: 95% DI water dip. Base pressure was kept around $1x10^{-6}$ mbar and ZnO target was used with ~99.999%. Pure argon (99.999% purity) was used as sputtering gas with constant flow of 60 sccm to create plasma. During deposition of RF power, chamber pressure and substrate temperature were maintained at 150 W, 2 x 10^{-2} mbar and 600 ºC respectively. Target to substrate distance was fixed around ~14 cm and deposition time was kept 2 hrs and 15 mins. For optimization of ZnO NRs, surface morphology and structural characterizations of the NRs were studied using field emission scanning electron microscopy and X-ray diffraction. Near-band and visible-range emission spectra were acquired using cathodoluminescence (CL) spectroscopy apparatus coupled with the FESEM, and operated at 7 nm bandwidth (~0.06 eV at 3.24 eV). Then, Circular dots of 500 µm diameter and 200 nm thick Au and Pd Schottky contacts were deposited by thermal evaporation with the help of physical mask. Spacing between two circular dots was around ~500 µm. Nanosensor devices were characterized in vacuum chamber with 2 x 10^{-3} mbar base chamber pressure and external heater was applied to vary the temperature from 50 to 175 ºC. The measurements were performed for Au/ZnO NRs nano-sensors with 1% and 5% hydrogen in argon concentrations, which falls below and above the explosive limit (4%) of hydrogen in air. For Pd/ZnO NRs nano-sensors, hydrogen concentration various from 5ppm to 1% hydrogen concentration. Table 6.1 shows deposition and gas sensing parameters for Au and Pd schottky contacted ZnO NRs based nanosenors.

Table 6.1: Deposition and gas sensing parameters for Schottky contacted ZnO NRs based nano-sensors

Substrate	2 inch n-Si (100)
Sputtering target	ZnO (99.999% purity)
Base pressure	1×10^{-6} mbar
Deposition pressure	2×10^{-2} mbar
Deposition time	2.15 hour
RF power	150 W
Sputtering gas	Argon (60 sccm)
Substrate temperature	600 °C
Target to substrate distance	14 cm
Metallization technique	Thermal evaporation
Metal contact	Au and Pd (500 µm dia., 200nm thickness) Spacing between two metal contacts ~500 µm
Gas sensor operating temperature	50°C, 75°C, 100°C, 125°C, 150 °C, 175°C
Hydrogen concentration	5ppm to 1% , 5% (in pure argon)

6.3 CHARACTERIZATION OF ZnO NRS

Surface morphologies of ZnO NRs were investigated by FESEM and AFM characterization as reviewed in chapter 4. Figure 6.1 (a-c) shows top view, tilted view (17° off normal) and cross sectional view (87° off normal) of NRs and from the FESEM images it can be observed that the NRs were well-aligned and uniformly distributed throughout the Si substrate. Height, average diameter and distribution density of NRs were determined to be ~850 nm, ~76 nm and ~1.5×10^{10} cm^{-2}, respectively. For further testifying these FESEM results, average size, density and distribution of ZnO NRs were also verified by AFM and shown in Figure 6.1 (d). It becomes very clear that deposited ZnO NRs by RF sputtering are aligned and has uniform circular rods with diameter ~76 nm. These nanorods also have high aspect ratio that makes it suitable for hydrogen nanosensors.

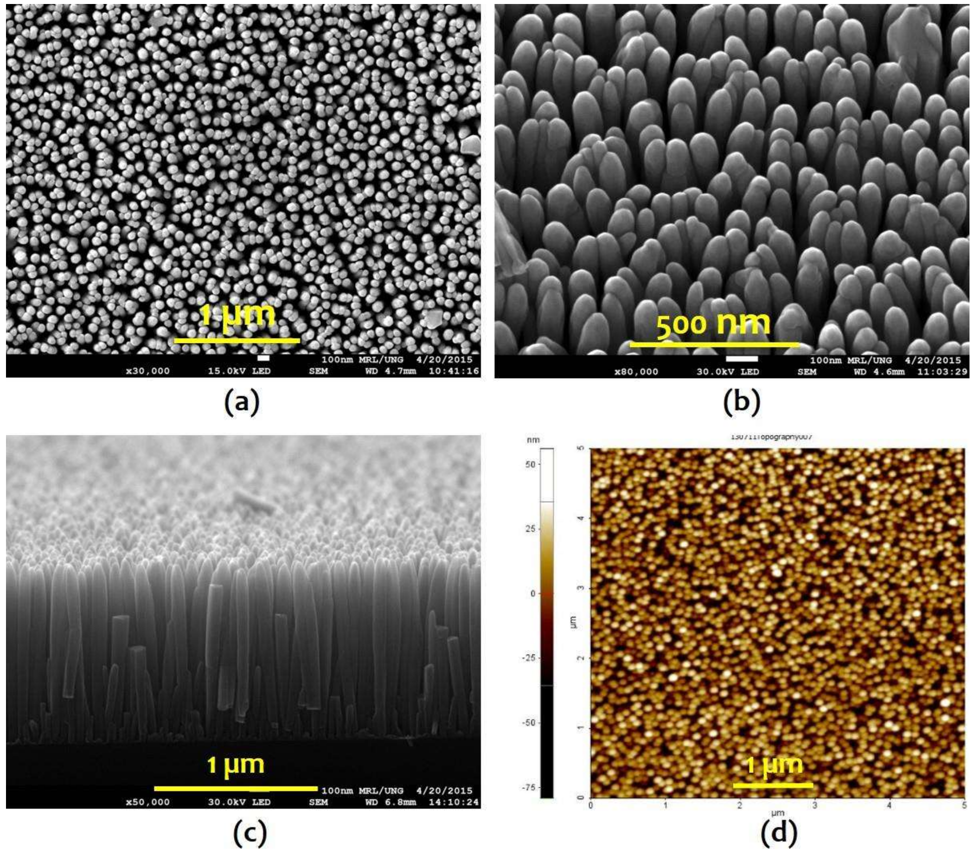

Figure 6.1: (a) Top view, (b) Tilted view (17° off normal), (c) Cross sectional View (87° off normal) of FESEM images and (d) AFM 2D image

Furthermore, structural characterization gives information about crystallinity and structural growth of deposited ZnO nanorods. Figure 6.2 shows 2θ-ω scan of XRD which depicts only one strong peak at 34.64° corresponding to (0002) growth direction indicating single crystal growth of ZnO NRs with hexagonal wurtzite structure of ZnO nanorods [Sun *et al.*, 2004]. (0002) peak shows full width half maxima (FWHM) ~0.21° and confirms highly crystalline growth. Finally, XRD and FESEM characterization clearly indicates that ZnO NRs have been grown in vertical plane along (0002) direction.

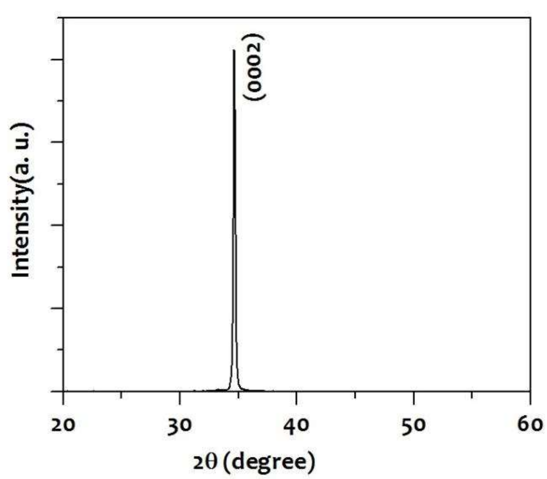

Figure 6.2: 2θ-ω scan of X-Ray diffraction pattern of ZnO NRs

Moreover, crystalline growth of ZnO nanorods was also confirmed using optical characterization. Figure 6.3 depicts room temperature CL spectra in which a strong peak is observed at 3.24 eV with FWHM ~0.13 eV corresponding to near band-edge emission (NBE) peak, which is attributed to recombination of free exciton [Myroniuk *et al.*, 2014]. Presence of a strong and sharp NBE peak and the absence of broad peak in visible range indicated high optical properties of ZnO NRs with insignificant density of traps/defects centers [Chandrinou *et al.*, 2009].

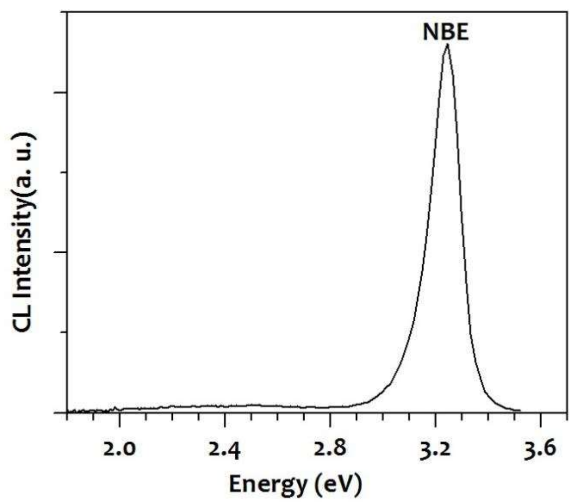

Figure 6.3: Room temperature CL spectra of ZnO NRs

6.4 SCHOTTKY CONTACTED Au/ZnO NRs BASED SENSOR FOR HYDROGEN SENSING

Hydrogen gas sensing properties of nanosensor were measured at two Au Schottky contacts as shown a schematic diagram in Figure 6.4 (a). These nanosensor have four Schottky contacts, two between Au and ZnO NRs and two between NRs and Si substrate. Schottky barrier height between Au/ZnO NRs and ZnO NRs/n-Si was determined using electron affinity model (EAM). The Schottky barrier height at Au/ZnO is $\phi_B=\phi_M-\chi_{ZnO}$ and conduction band and valance band offsets at ZnO/Si are $\Delta E_C=\chi_{ZnO} - \chi_{Si}$ and $\Delta E_V=E_{g,ZnO} - E_{g,Si} + \Delta E_C$. For Au, ϕ_M =5.1 eV, χ_{ZnO}=4.35, χ_{Si}=4.05, $E_{g,ZnO}$=3.24 eV , $E_{g,Si}$=1.12 eV [Ranwa *et al.*, 2014].The resulting value for Schottky barrier height is ϕ_B~0.78 eV and conduction band offset is ΔE_C ~0.3 eV.

Figure 6.4 (b) depicts I-V characteristics of Au/ZnO NRs/Si/ZnO NRs/Au schottky junction at 75 °C without hydrogen and with 1% and 5% hydrogen concentration. I-V plot shows rectifying behavior due to presence of schottky junction at ZnO/Si and Au/ZnO heterojunction. With exposure of 1% and 5% hydrogen concentration in argon, schottky barrier height decreases and enhances current and lateral voltage shift in comparison to air. As hydrogen concentration is increased, enhanced adsorption/desorption reactions on HJ and ZnO NRs surface takes place and enormous change in depletion region occurs which shows that current increases with increase in hydrogen concentration in nano devices even at same operating temperature.

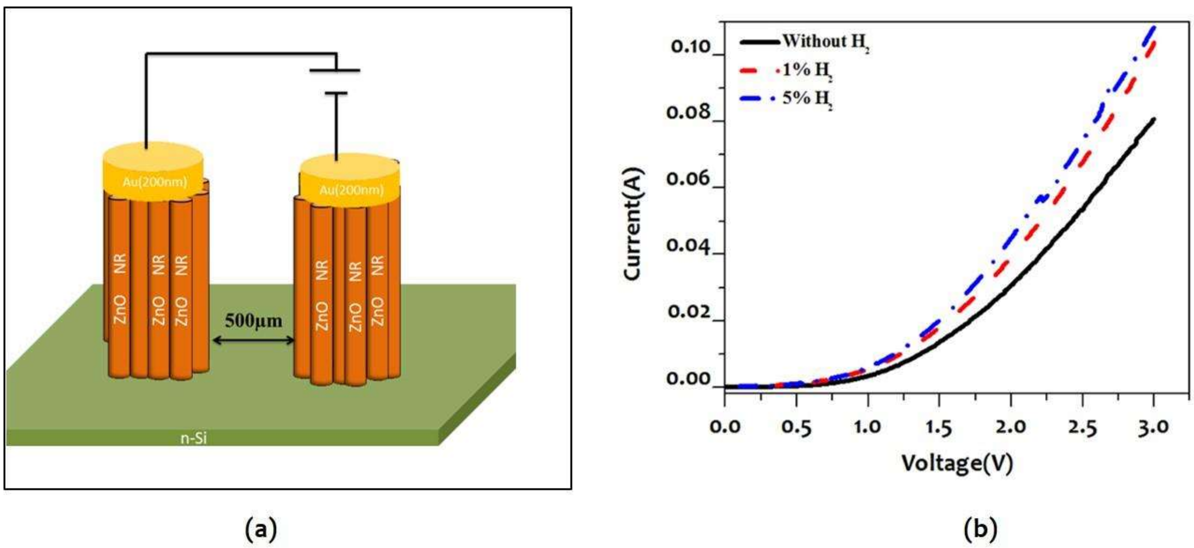

Figure 6.4: (a) Schematic diagram of nanosensor, (b) I-V Characteristics of nanosensor at 75 °C without and with 1% and 5% H_2 concentration

For further investigation, resistance response curve with time gives information about repeatability of hydrogen sensor response cycle. Figure 6.5 (a-b) shows resistance response curve with time of Au/ZnO NRs/Si/ZnO NRs/Au heterojunction based nanosensor device at 100 ºC operating temperature for 1% hydrogen and 5% hydrogen in pure Argon concentration, respectively. The flammability limit of hydrogen is around 4% in air and the testing concentration was chosen below and above this limit. The curve clearly shows that resistance changes can be affected by hydrogen concentration at particular operating temperature. It can also be noticed that change in resistance is dominant up to a certain level of hydrogen concentration only, beyond which, the rate of increase gets slow gradually becoming saturated for constant operating temperature.

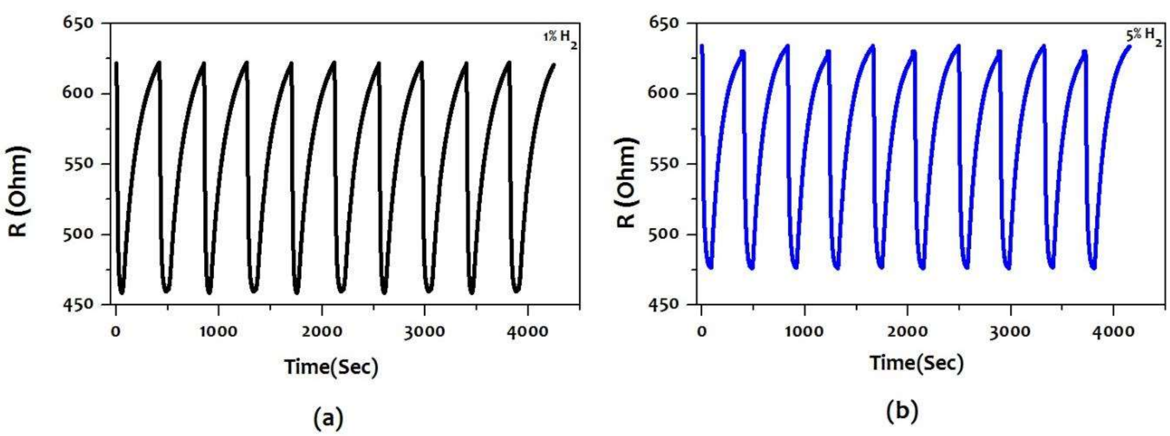

Figure 6.5: Resistance response curve with time at 100 °C for (a) 1% and (b) 5% H_2 concentration, respectively

Operating temperature always plays a key role in hydrogen sensing so it's become necessary to study temperature depended gas sensor response for various hydrogen concentration. Temperature dependent resistive response of the nano-sensor in 1% and 5% hydrogen in pure argon concentration is shown in figure 6.6 (a-b).

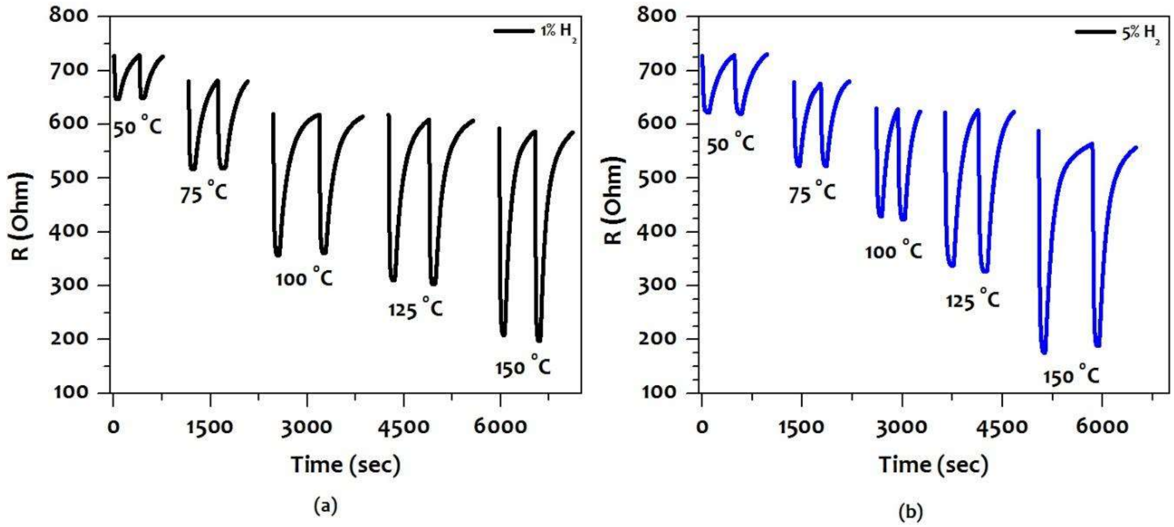

Figure 6.6: Temperature dependent resistive response curve: (a) 1% Hydrogen and (b) 5% Hydrogen in argon

As operating temperature increase from 50 °C to 150 °C, rate of adsorption/desorption reaction of reactive gases increases with temperature. From the figure, it can be seen that the base resistance decreases with increasing operating temperature. This is due to following two reasons; (i) the resistance decreases with increasing temperature in the semiconductors, and (ii) Schottky barrier height also decreases with temperature which further reduces the resistance. Change in resistance was observed to be relatively lesser for 5% in comparison to 1% hydrogen at particular operating temperature due to the saturation of response. Schottky metal junctions such as Pt, Pd and Au enhances the gas sensitivity of ZnO NR based gas sensors [Rout *et al.*, 2007]. In present work, ZnO NR, Au/ZnO NRs and ZnO NRs/Si Schottky junctions play an important role in hydrogen sensing as adsorption/desorption of reactive gases take place at ZnO NRs and at Schottky junction. On exposure to hydrogen gas, adsorption/desorption process take places at Au/ZnO Schottky junction and Au act as catalyst for hydrogen adsorption alike Pt and Pd metals [Pandis *et al.*, 2007]. In gas sensing, hydrogen molecule gets diffused in Au electrodes, causes variation of barrier height at Au/ZnO junctions and increase sensitivity. Gas sensor performance is based on its characteristics like response time, recovery time and relative response curve. Exponential increase in resistance allows evaluation of recovery/rise time (τ_r). Whereas, exponential decrease in resistance allows evaluation of response/decay time (τ_d), as given: [Adamyan *et al.*, 2009]

$$R = R_0 + A\exp\left(\frac{t}{\tau_r}\right) \tag{6.1}$$

$$R = R_1 + B\exp\left(-\frac{t}{\tau_d}\right) \tag{6.2}$$

where A and B are scaling constant. Rise and decay times were extracted from experimental data by exponential fitting. Figure 6.7 (a-d) Show Resistive Response Curve with recovery and response time exponential fitting for 1% Hydrogen and 5% Hydrogen Concentration at 100 ºC, respectively.

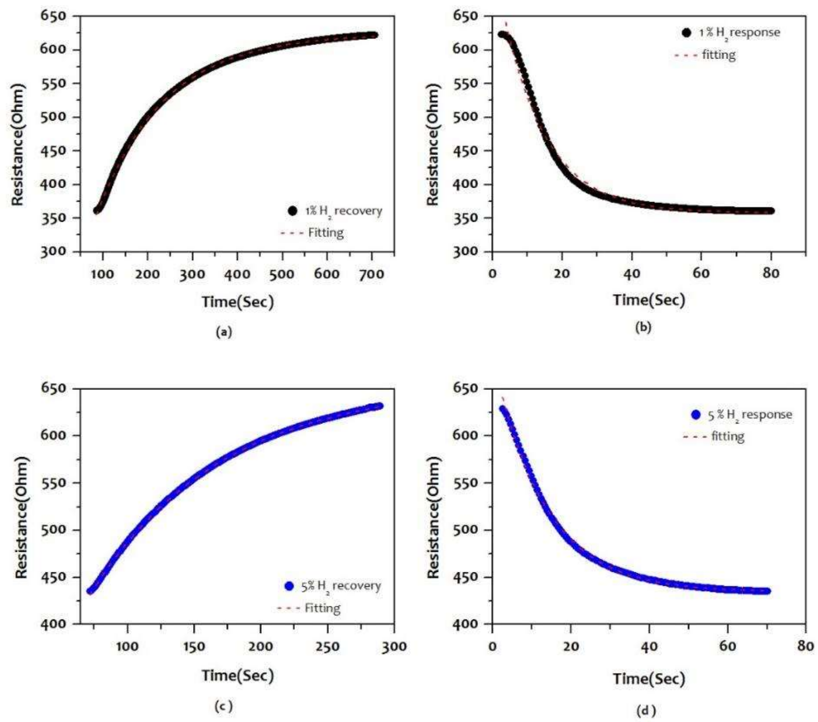

Figure 6.7: (a- d) Resistive response curve with recovery and response time exponential fitting for 1% H_2 and 5% H_2 concentration at 100 °C, respectively

Calculated response and recovery time with change in temperature for 1% and 5% hydrogen concentration have been shown in Figure 6.8 (a-b). Table 6.2 shows response and recovery time with different operating temperature. Response time increases from 9.4 sec. to 12 sec. for 1% hydrogen with temperature for low temperature range (up to 100 ºC) and then almost remains constant in temperature range from 100 to 150 ºC. For 5 % hydrogen, due to relatively higher concentration, response time decreases with increasing temperature (up to 100 ºC) from 16 to 12 sec and for higher operating temperature, it becomes almost constant. Recovery time is highly influenced by operating temperature and varies from approximately 200 sec. to 120 sec. for 1% hydrogen concentration as operating temperature is changed from 50 to 150 ºC. At higher hydrogen concentration (5%), the dependency on temperature variation is more evident. With increase in operating temperature, more oxygen ions are adsorbed at ZnO NRs and creates a depletion region. During hydrogen loading process, these hydrogen molecules react with oxygen species and shrinks the depletion region. The resulting fast recovery is due to availability of large number of free electrons. At operating temperature 100 ºC, nanosensor shows recovery time of around ~150 sec. for 1% hydrogen and around ~100 sec. for 5% hydrogen concentration. Large change in recovery time with hydrogen concentration depicts that more ions of hydrogen reacts with oxygen ions and further decreases the depletion region.

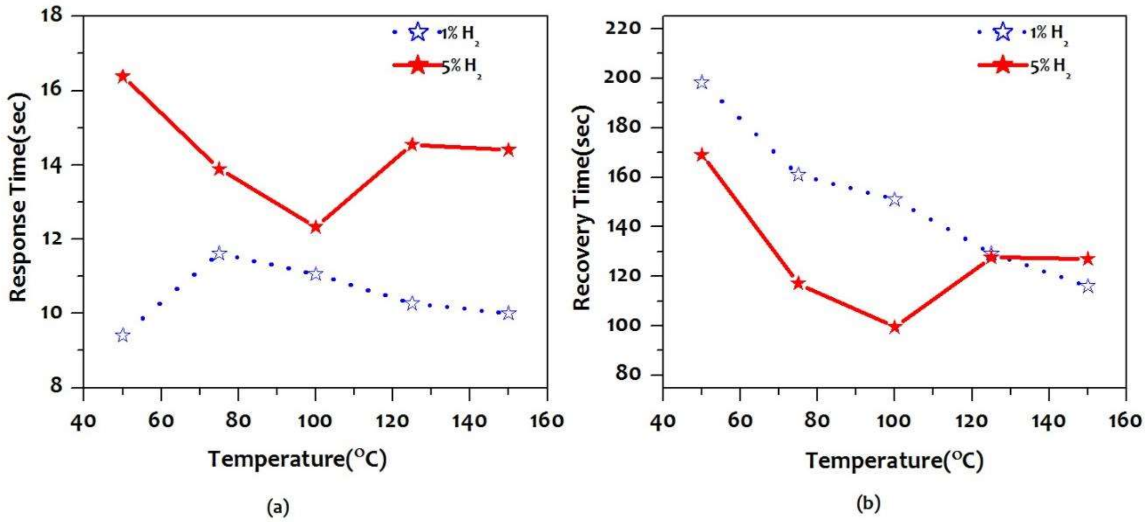

Figure 6.8: (a) Response Time, (b) Recovery time of nano- sensors in presence of 1% and 5% hydrogen with change in temperature from 50 °C to 150 °C

Table 6.2: Response and recovery time with operating temperature

Operating temperature (°C)	Response Time (1% H_2)	Recovery Time (1% H_2)	Response Time (5% H_2)	Recovery Time (5% H_2)
50 °C	9.4 Sec	198.4 Sec	16.4 Sec	169.1 Sec
75 °C	11.6 Sec	161.1 Sec	13.9 Sec	117.0 Sec
100 °C	11.0 Sec	151.1 Sec	12.3 Sec	99.5 Sec
125 °C	10.3 Sec	129.9 Sec	14.6 Sec	127.7 Sec
150 °C	10.0 Sec	116.0 Sec	14.4 Sec	127.0 Sec

Gas sensitivity/relative response is the relative change in resistance with respect to resistance in presence of air and is given [Lupan *et al.*, 2010]:

$$\text{RelativeResponse} = \left(\frac{R_a - R_g}{R_a}\right) \times 100\% \tag{6.3}$$

Relative sensor response with temperature curve at different hydrogen concentrations is shown in Figure 6.9 which clearly indicates that sensitivity increases linearly with operating temperature. Sensitivity increases from 11 to 67 ± 2% with increase in operating temperature from 50 °C to 150 °C. The variation in sensitivity behavior is very low for 1% and 5 % hydrogen concentration due to saturated NRs and Schottky contact. Beyond 1% hydrogen concentration, sensitivity does increase with temperature, but not drastically. Relative change in resistance is 41 ± 2% and 34 ± 2% for 1% and 5% hydrogen concentration at 100 °C, respectively. The above results suggest that nanosensor shows fast response time (9-12 sec) and moderate sensitivity (11 to 67 ± 2%) at operating temperature below 150 °C. Recent studies revealed that Au/ZnO nanorods with Schottky junction based nanosensor shows fast response time as compared to undoped/doped ZnO nano structure at low operating temperature. Hassan *et al.* in [Hassan *et al.*, 2013] displayed that Pt/ZnO nanorods based sensor showed 200 sec response time with high sensitivity at 100 °C. Alam *et al.*, in [Alam *et al.*, 2015] also conveyed that Pd nanocubes decorated ZnO nanorods based hydrogen sensor gave high response time of 1.98 min. at 100 ºC for 1% hydrogen concentration.

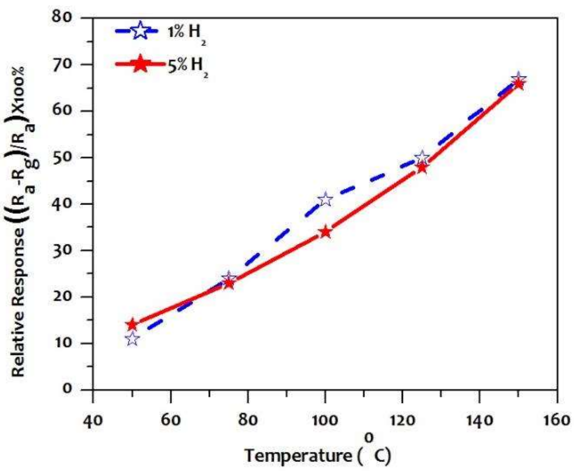

Figure 6.9: Sensor's relative response versus temperature curve for varying hydrogen concentration

6.5 PROPOSED GAS SENSING MECHANISM

Figure 6.10 (a), (b) shows schematic diagram of proposed gas sensing mechanism and Figure 6.10 (c), (d) exhibits energy level diagram of Au/ZnO NRs interface in presence of hydrogen at forward and reverse bias, respectively.

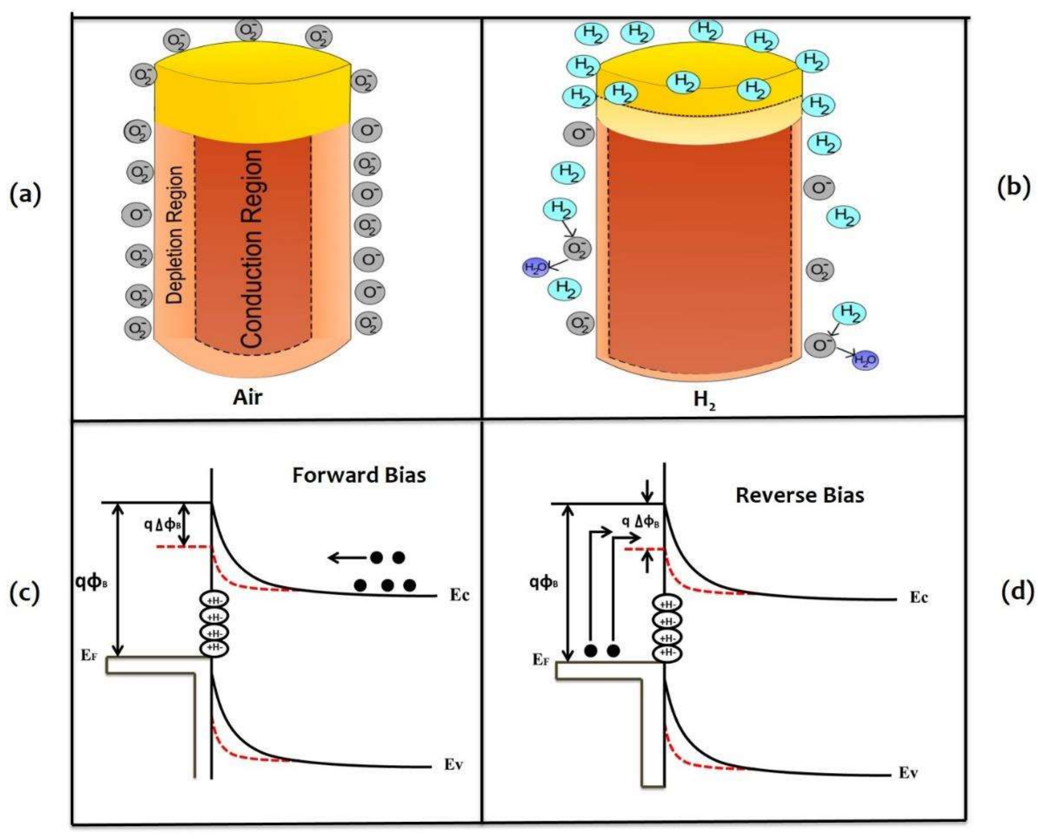

Figure 6.10: (a), (b) Proposed gas sensing mechanism and (c), (d) Forward and reverse bias energy band diagram at Schottky junction

When ZnO NRs comes in contact with atmospheric oxygen and gases, oxygen molecules get adsorbed on ZnO NRs surface and extract electron from conduction band. This phenomenon creates adsorbed oxygen (O^-, O_2^-, O^{2-}) ions on nanorods surface and form a depletion region in nanorods as discussed earlier. Adsorption of oxygen decreases electron concentration in ZnO NRs and results in increase in resistance of the device. But when ZnO nanorods are exposed to hydrogen, H_2 molecules react with adsorbed oxygen, increasing electron concentration in conduction band and in turn, decreasing the resistance of ZnO nanorods. These chemisorbed reactions are influenced by hydrogen concentration and are highly temperature dependent as well. For low temperature and for low hydrogen concentration, Schottky junctions plays an important role, and due to the adsorption of hydrogen molecules at Schottky junction, barrier height changes [Yu *et al.*, 2009]. When hydrogen molecules react with Au contact, they get dissociated into hydrogen atoms [Pandis *et al.*, 2007]. Dissociated hydrogen atoms then forms a dipole coating at Au/ZnO NR interface layer and creates electric field at junction and reduces effective barrier height and metal work function due to hydrogen atom diffusion. In forward bias, at Au/ZnO NRs junction, electrons use dipoles as tunnelling junctions and increase current on one hand and on the other, reduce resistance at junction. In reverse bias state, presence of such dipoles requires a low reverse bias voltage to cross the barrier height via tunnelling. This variation in barrier height increases the conductivity of Au/ZnO NR heterojunction in comparison to ohmic contact. Summing up, as gas sensitivity and recovery time are highly affected by reactions taking place at ZnO NRs surface and at Schottky junctions, nanosensor's performance is highly influenced by Schottky barrier height and hydrogen loading/deloading induced variation in depletion width of ZnO NRs.

6.6 SCHOTTKY CONTACTED Pd/ZnO NRs BASED NANOSENSORS

So far in this chapter, critical role of Schottky contact in ZnO NRs based hydrogen sensor have been explained that enhances hydrogen sensor's relative response to a large extent. Firstly, Au/ZnO NRs based nano-sensors are optimized. For further enhancement of the sensor's relative response with lower detection limit for hydrogen gas at low operating temperature, Pd contacted ZnO nanorods based hydrogen sensors have also been studied. These sensors have similar device structure as of Au/ZnO NRs based hydrogen sensor. In comparison to Au and Pt transition metals, Pd has higher tendency to react with reducing gases and exhibit large change in Schottky barrier height than other transition metals [Zhang *et al.*, 2015; Roy *et al.*, 2016; Xing *et al.*, 2011; Basu and Dutta, 1997]. For hydrogen sensing, Pd/ZnO NRs based hydrogen sensors are exposed to various hydrogen concentration ranging from 5 ppm, 10ppm, 50ppm, 100ppm, 500ppm, 1000ppm to 1% hydrogen in pure argon. Sensor's operating temperature is also varied from 50 °C to 175 °C with incremental step of 25 °C. Figure 6.11 depicts relative response curve with time for various hydrogen concentration starting from 5ppm to 1% hydrogen with increasing operating temperature from 50 °C to 175 °C.

From earlier sections, it can be clearly seen that the key factors like hydrogen concentration and operating temperature highly influences sensors response. During loading/deloading of hydrogen in test chamber, change in sensor's resistance is measured which is due to change in depletion region of ZnO NRs and Schottky barrier height variation. Relative response curve for Pd/ZnO NRs based hydrogen sensor shows increasing sensor response with increase in hydrogen concentration from 7ppm to 1% (in pure argon) at constant operating temperature. Even at 50 °C low operating temperature, sensor demonstrates relative sensor response varying from 13.8% to 37.13% as hydrogen concentration increases from 7ppm to 1%. These Pd/ZnO nanorods based hydrogen sensors are able to achieve high sensors response of ~13.8 % even for 7 ppm hydrogen concentration at 50 °C operating temperature which was not possible with Au/ZnO NRs based hydrogen sensors. When Pd transition metal comes in contact with hydrogen gas, hydrogen molecules get diffused into metal, creates dipole at heterojunction and PdH_x is formed [Johansson *et al.*, 2010; Phan and Chung, 2015]. Due to induced electric field at junction, Schottky barrier height reduces. As operating temperature increases from 50 °C to 150 °C, it enhances surface adsorption/desorption reactions which in turn, increases sensor's response. For lowest hydrogen concentration of 7ppm, sensor response varies from 13.86 % to 38.47 % when operating temperature is increased from 50 °C to 150 °C. With presence of Pd Schottky contact, highest sensors relative response of 91.26 % is achieved for 1% hydrogen (below 4% ignition limit) at 175 °C operating temperature.

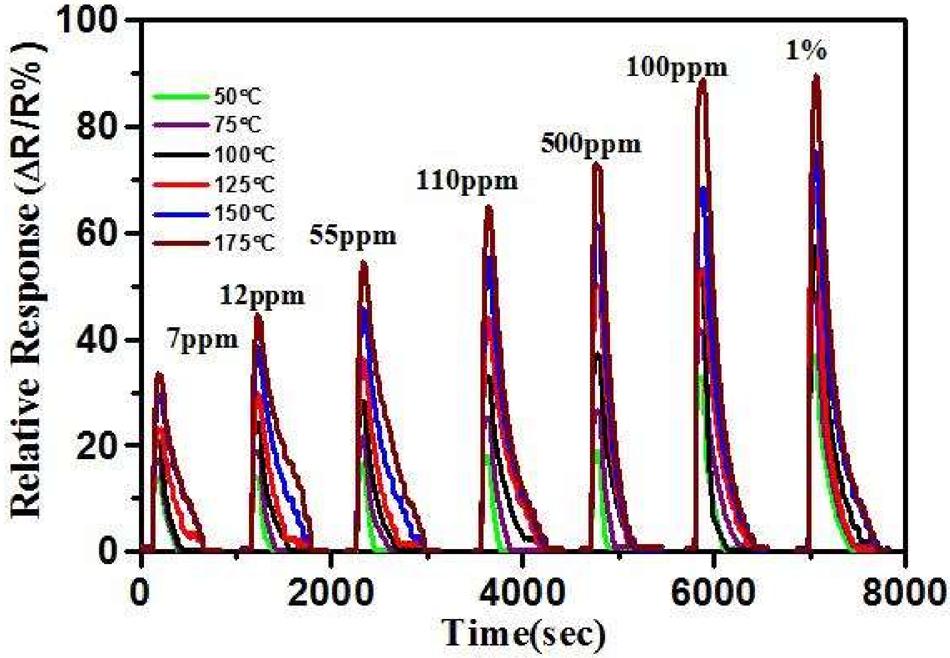

Figure 6.11: Relative response curve with time for various hydrogen concentration ranging from 7 ppm to 1% (in Pure Argon) with increasing operating temperature from 50 °C to 175 °C

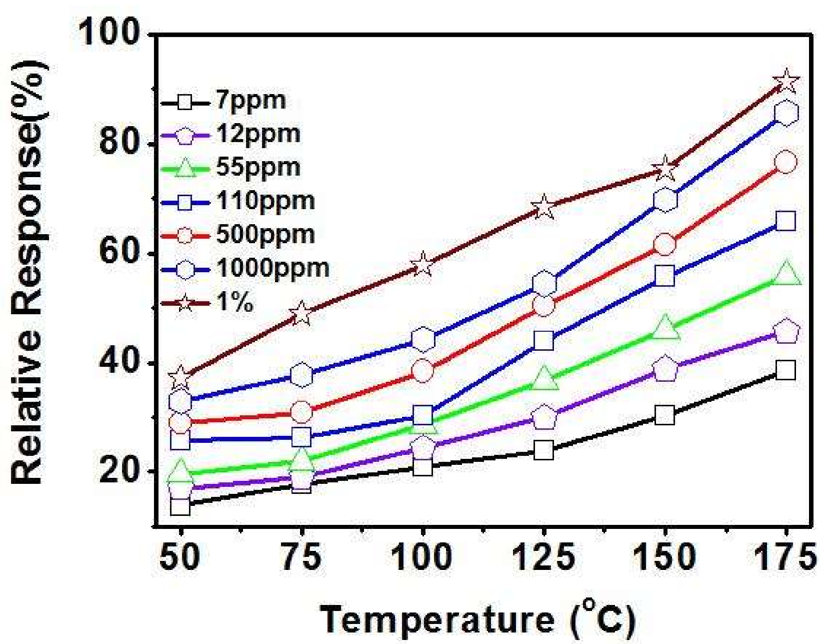

Figure 6.12: Sensors relative response with operating temperature ranging from 50 °C to 175 °C for 5ppm to 1% hydrogen concentrations

Figure 6.12 shows sensor's relative response at various operating temperature for 7 ppm to 1% hydrogen concentrations. Sensor's relative response at each hydrogen concentration with operating temperatures ranging from 50 °C to 175 °C gives enhanced response. As hydrogen concentration is increased from 7 ppm to 1%, it enhances chemisorbed reaction rates which changes depletion region and largely decreases sensor's resistance. Due to presence of higher hydrogen concentration, hydrogen diffusion rate is also higher in transition metal Pd and as a result, Schottky barrier height also decreases which further decreases sensor's resistance in comparison to presence of oxygen in the chamber. Thus, at low operating temperature ranging from 50 °C to 75 °C, sensors response varies from 13.8-38.7% to 17.8-48.93% for 7 ppm to 1% hydrogen concentration. At increasing operating temperature from 50 °C to 175 °C, sensor's response increases from 37.13% to 91.26% for 1% hydrogen concentration which is higher than Au/ZnO NRs based hydrogen sensor's relative response. Thus, Pd/ZnO NRs based hydrogen sensors show high sensor relative response with fast response and recovery time. Response and recovery time have been calculated by equations 6.1 and 6.2. Figure 6.13 gives (a) Response time, and (b) Recovery time for various hydrogen concentrations from 5ppm to 1% at 100 °C and 150 °C, respectively. Pd/ZnO nanorods based hydrogen sensors shows fast response of ~ 8 to 20 Sec with moderate recovery time ranging between 70 Sec to 300 Sec for 7 ppm to 1% hydrogen concentration with 100 °C to 150 °C operating temperature.

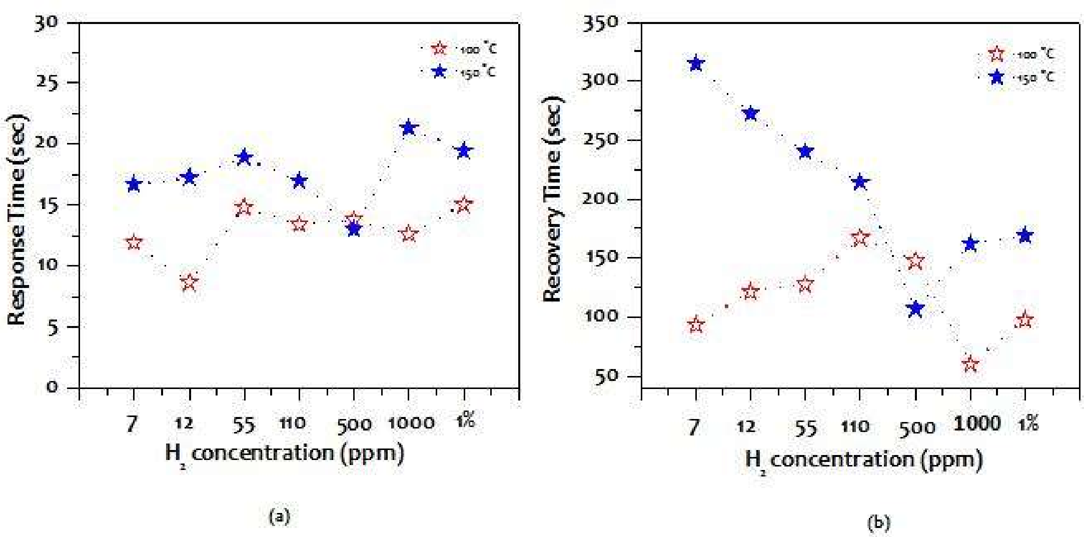

Figure 6.13: (a) Response Time, and (b) Recovery Time for various hydrogen concentration ranging from 7 ppm to 1% at 100 °c and 150 °c, respectively

6.7 HIGH SELECTIVITY OF Pd/ZnO NRs BASED HYDROGEN SENSORS

Selectivity is one of the important key parameter for efficient gas sensor application. ZnO nanorods based sensor shows response to various gases such as CH_4, H_2S, CO_2, H_2 and hydrocarbons [Hong *et al.*, 2016; Ren *et al.*, 2011; Mondal *et al.*, 2014; Ling *et al.*, 2016; Kotoch *et al.*, 2016; Yuliarto *et al.*, 2015]. Although Pd/ZnO NRs based sensor shows high relative response to hydrogen gas with good stability at moderated operating temperature. To make sensor sustainable in contaminated environment, high selectivity is desirable. Thus, high selectivity for Pd/ZnO nanorods based sensor is achieved by exposing it to various gases such as H_2, methane (CH_4), H_2S and CO_2 at various gases concentration ranging from 7ppm to 10000 ppm (1%) at 150 °C operating temperature. As we know that ZnO can sense wide range of oxidizing and reducing gases, hence, Pd/ZnO NRs based sensor shows response with these gases which strongly depends on gas concentration (lower limit of detection), operating temperature range variation. Figure 6.14 (a-c) shows relative response curve with time for CH_4, H_2S and CO_2 gases for various gases concentration and operating temperature and (d-f) shows sensor's response with operating temperature variation at various gas concentration for CH_4, H_2S and CO_2 gases.

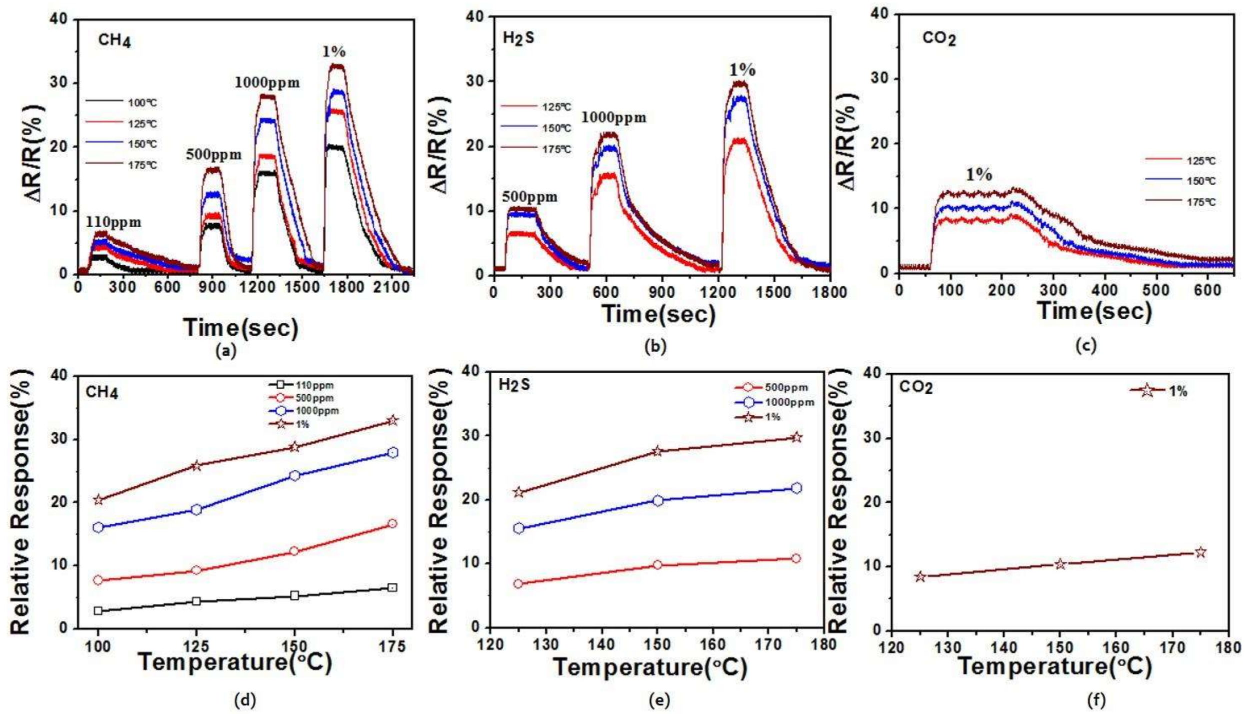

Figure 6.14: (a-c) Relative response curve with time and (d-f) Sensors response with operating temperature variation for CH_4, H_2S and CO_2 gases for various gases concentration while operating temperature varies from 100 °C to 175 °C

As both Pd/ZnO NRs Schottky junction and ZnO NRs takes part in gas sensing mechanism, when Pd/ZnO NRs based sensor is exposed to CH_4 gas with concentration varying from 110 ppm to 1% concentration in pure argon gas, relative response varies from ~2.7 % to 33% with operating temperature ranging from 100 °C to 175 °C. In comparison to CH_4 gas, when sensor is exposed to H_2S gas, minimum detection limit observed is 500 ppm gas concentration at 125 °C. When operating temperature increases from 125 °C to 175 °C and gas concentration from 500 ppm to 1%, sensors response varies from 6.8% to 29.5 %. When sensor is exposed to CO_2 gas, sensors response is obtained at operating range from 125 °C to 175 °C for lower limit of CO_2 gas concentration at 1% in pure argon gas. So, it is clearly observed that in above mention gases, CH_4 gas shows maximum response even for 100 °C operating temperature and at 100 ppm gas concentration in comparison to H_2S gas which responds to minimum concentration of 500 ppm at 125 °C. In these gases responses, Pd Schottky contact barrier height and ZnO NRs depletion region varies when gas is exposed to the sensor. As CH_4 gas's bond breaks at ~100 °C operating temperature, hydrogen molecule gets diffused into Pd as discussed in hydrogen sensing mechanism where it reduces Schottky barrier [Hong *et al.,* 2015]. Besides this, for H_2S gas which high stable at low operating temperature, change is observed only in depletion region of ZnO NRs which requires higher concentration of ~500 ppm with 125 °C operating temperature to show sensors response. The gas response increases as operating temperature and gas concentration increases when sensor is exposed to CO_2 gas which is highly stable and have high molar mass in comparison to other gases. Therefore, it is observed that minimum gas concentration of 1% is required to show sensor response of 9% at 125 °C operating temperature. As operating temperature increases, sensor response increases from 9% to 11 %.

Thus, to study sensors selectivity, relative response with various gas concentration and gases (CH_4, H_2S, H_2 and CO_2) have been plotted at 175 °C operating temperature. Pd/ZnO nanorods based sensor shows change in resistance at 175 °C operating temperature for various gases and gives relative response curve for each gas concentration. Figure 6.15 shows selectivity properties of Pd/ZnO NRs based sensors for CH_4, H_2S, CO_2 and H_2 gases at the concentration of 7 ppm, 12 ppm, 55 ppm, 110 ppm, 500ppm, 1000 ppm and 10,000 ppm, respectively at 175 °C operating temperature.

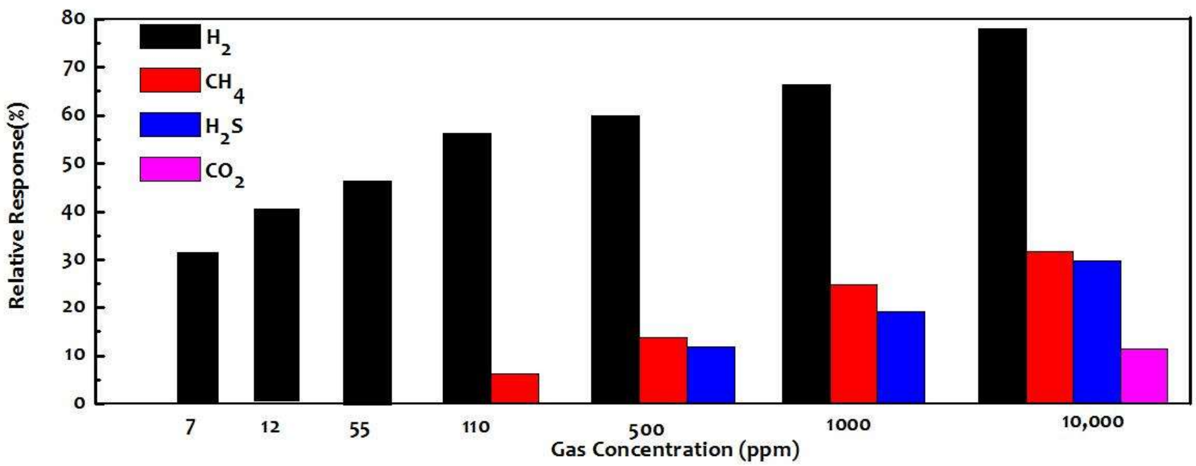

Figure 6.15: Selectivity properties of Pd/ZnO NRs based sensors for CH_4, H_2S, CO_2, H_2 gases, at concentration of 7 ppm to 10,000 ppm (1%), respectively at 175 °C operating temperature

It can be clearly derived from the results that Pd/ZnO NRs based sensors shows high response for hydrogen in comparison to other gases. Such sensor is highly selective only for hydrogen gas even at low concentration of 5ppm and does not sense other gases. For Pd/ZnO NRs based sensors, minimum concentration is 110 ppm for CH_4 gas, 500 ppm for H_2S gas and 1% (10,000 ppm) for CO_2 gas. These sensors also show relative response ~ 32% for 7 ppm hydrogen concentration, 10% for 110 ppm CH_4, 12.8 % for 500 ppm H_2S and 11% for CO_2 gas concentration at constant operating temperature 175 °C. As earlier discussed, smaller hydrogen molecules show high surface reaction and gets diffused largely into Pd metal in comparison to other gases, Schottky barrier height gets highly affected in presence of hydrogen in comparison to other reducing gases. Thus Pd/ZnO NRs based hydrogen sensors are highly selective towards hydrogen gas with lower limit of detection of about 5ppm.

6.8 CONCLUSION

In conclusion, Schottky contacted ZnO NRs shows high sensors response with fast response and recovery time and moderate operating temperature. Initially, Au/ZnO NRs based hydrogen sensor fabricated which tested in 1% and 5% hydrogen concentration environment at operating temperature ranging from 50 °C to 150 °C. Sensors relative response highly dependent on operating temperature and varies from 11% to 67 % for both hydrogen concentration as operating temperature varies from 50 °C to 150 °C. These sensors give fast response ~ 14 s for 1% hydrogen and 12.8 s for 5% hydrogen at operating temperature 100 °C. The recovery times were determined ~100 and 150 s for 1% and 5% hydrogen concentrations, respectively. For further enhancement of sensors response for low hydrogen concentration and low operating temperature, Pd/ZnO NRs based sensors were fabricated. Because of change in Schottky barrier as well as in depletion region of ZnO NRs in presence of hydrogen gas, sensors show ~13.8 % to 91.26% sensors response for 7 ppm to 1% hydrogen concentration variation with operating temperature ranging from 50 ºC to 175 ºC. These sensors show high selectivity towards hydrogen (32% response at 175 ºC) in comparison to other gases like CH_4, H_2S, CO_2. Minimum limit of detection for hydrogen is 7 ppm (32 % at 175 ºC) in comparison to 110 ppm CH_4 (10%), 500 ppm H_2S (12.8%) and 1% CO_2 (11%).

…