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Pd/ZnO nanorods based sensor for highly selective detection of extremely low concentration hydrogen

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We report highly hydrogen selective Pd contacted ZnO nanorods based sensor detecting low concentration even at low operating temperature of 50 °C. The sensor performance was investigated for various gases such as H_2, CH_4, H_2S and CO_2 at different operating temperatures from 50 °C to 175 °C for various gas concentrations ranging from 7 ppm to 10,000 ppm (1%). The sensor is highly efficient as it detects hydrogen even at low concentration of ~7 ppm and at operating temperature of 50 °C. The sensor's minimum limit of detection and relative response at 175 °C were found 7 ppm with ~38.7% for H_2, 110 ppm with ~6.08% for CH_4, 500 ppm with ~10.06% for H_2S and 1% with ~11.87% for CO_2. Here, Pd exhibits dual characteristics as metal contact and excellent catalyst to hydrogen molecules. The activation energy was calculated for all the gases and found lowest ~3.658 kJ/mol for H_2. Low activation energy accelerates desorption reactions and enhances the sensor's performance.

All living organisms in an ecosystem pertain to extreme consequences through the confined atmosphere, hence it is mandatory to monitor the level of gases and subsequently their effect on climate. Hydrogen is one of the explosive gas and have huge potential applications such as reactant in hydrogenation for sulphur separation and nitrogen compounds in oil refinery, propulsion fuel of space flight, coolant in electrical generators in power plant, generation of ammonia for fertilizer industry and growth of epitaxial silicon from silicon tetrachloride[1–3]. Due to low ignition energy (0.02 mJ) and broad explosive range (4–75%) of hydrogen, safety precaution is highly recommended[4, 5]. High sensitivity, low power consumption, high selectivity and low cost are essential aspects of hydrogen sensor to detect leakages in industry as well as domestic sector[6–9]. Currently, resistive gas sensors are broadly employed due to their good performance, low cost and compatibility with electronic circuits[10]. However, the resistive gas sensors have some deficiencies such as poor selectivity and high operating temperature, which requires further advancement of these gas sensors[11]. To fabricate a highly selective sensor is still a prime task for researchers. Generally, a wide range of gases can interact with chemisorbed oxygen ions on to the surface of sensing layer and subsequently may create interference to the gas analyte which has to be detected surrounded by other gases. Thus, to prevent from the false signal of unwanted gas species, many reports have been published to rectify the issue of cross sensitivity in order to obtain highly selective sensor response by using various techniques such as (a) doping of transition metal into metal oxide[12–14], (b) decoration of noble metal nanoparticles over the metal oxide[15, 16], (c) employment of hybrid metal oxide sensing layers[17, 18], (d) altering the operating temperature[19, 20] and (e) use of filtering layers[21–23]. However, altering the operating temperature of sensing layer is more effective method to increase selectivity because of difference in adsorption energy and surface reactivity of various gas species but it also has some adverse effect such as the changing in grain size or surface structure of sensing layer due to higher temperature.

ZnO an n-type semiconductor, belongs to a direct band gap of 3.37 eV[24]. It has tremendous properties like high chemical and thermal stability and large exciton binding energy (60 meV)[25]. ZnO is also used for various gas detection such as H_2, NO_2, CH_4, CO_2, H_2S, NH_3 and volatile organic compounds. The ZnO based gas sensor's behaviour was highly influenced by surface morphology, dopant and operating temperature. 1-D nanostructures

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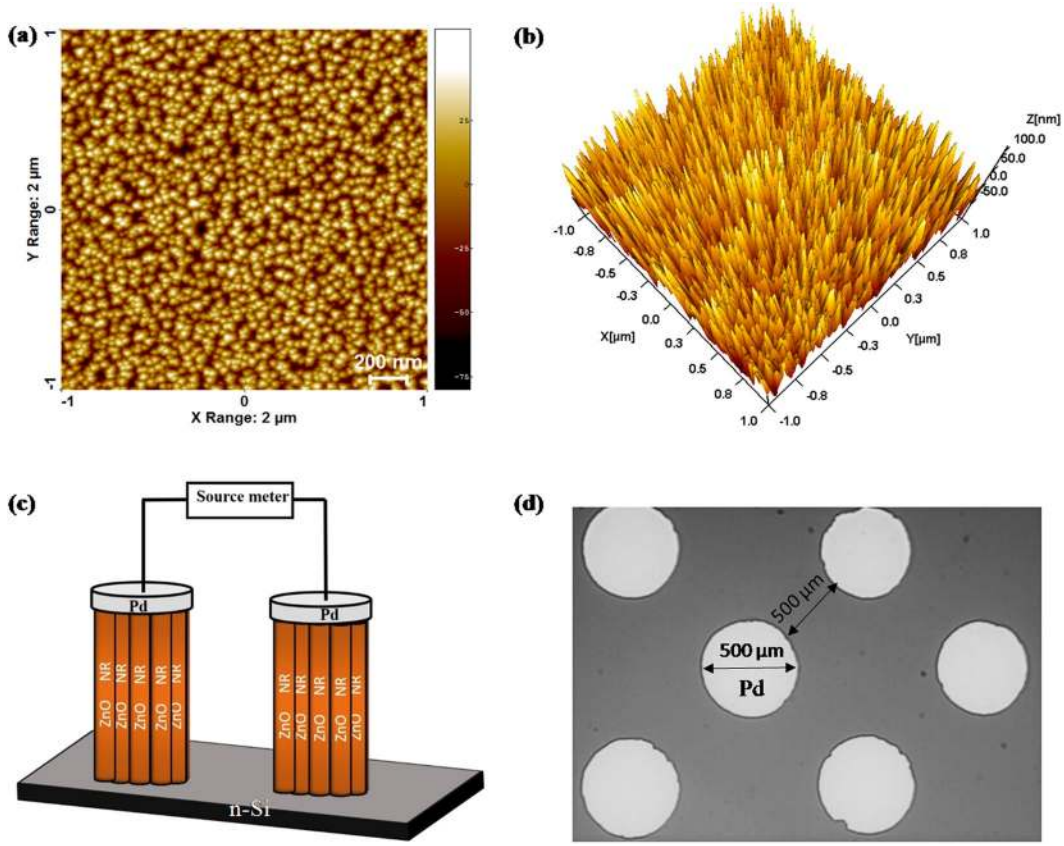

Figure 1. (**a,b**) 2-D and 3-D AFM images of ZnO NRs; (**c,d**) The schematic diagram and optical microscope image of the device.

such as nanotubes, nanorods (NRs), nanowires and nanoneedles shows high sensitivity than thin films because of high aspect ratio and higher diffusion of gases[26–28]. Resistive gas sensors with noble metals such as Pd, Pt and Au exhibit superior sensing response for hydrogen gas due to their catalytic activity and solubility of hydrogen atom[29,30]. Among them, Pd has been most studied in hydrogen sensor owing to its excellent capability of adsorption of hydrogen molecules and their dissociation into hydrogen atoms. Moreover, the diffusion of hydrogen atoms is accelerated throughout the surface and leads to increase the interaction with active sites of the surface[31]. Basu *et al.* has fabricated ZnO thin films based sensor (Pd/ZnO/p-Si and Pd/ZnO/Zn) and found highly hydrogen selective sensor in the range of 2000–20000 ppm H_2 concentration[32]. Lupan *et al.* fabricated single Cd doped ZnO nanowire using focused ion beam and H_2 was detected down to 100 ppm at room temperature with good sensitivity while poor response to CH_4, C_2H_5OH, O_2, LPG and NH_3[33]. Mondal *et al.* synthesized the ZnO-SnO$_2$ composite type hydrogen sensor for different concentration of tested gases at 150 °C and the cross sensitivity of this sensor to CH_4 and CO was not high at same temperature[34]. Ren *et al.* has prepared ZnO nanowires networks decorated with photo-decomposed Pd nanoparticles by CVD and obtained highly selective sensor response to 1000 ppm H_2 whereas C_2H_5OH, $(CH_3)_2CO$, NO_2, HCHO and NH_3 displayed the poor sensitivity[35]. Hong *et al.* reported highly selective PMMA-coated Pd nanoparticles/single-layer graphene hybrid sensor for H_2, owing to the selective H_2 filtration effect of the PMMA[23]. Many reports are available on hydrogen sensing by Pd nanoparticles decoration on the ZnO nanostructures, but only few reports are available by Pd contacted ZnO. Hence this work is carried out to explore further performance of Pd contacted ZnO nanorods based hydrogen sensor. Pd contacted vertically aligned ZnO NRs based sensors were fabricated by RF magnetron sputtering technique. Sensor's response were characterized in presence of various gases such as H_2, CH_4, H_2S and CO_2 at various concentration and operating temperature ranging from 50 °C to 175 °C. Gas sensing mechanism based on activation energy is discussed to explain high selectivity towards hydrogen gas in comparison to other gases.

Results

ZnO NRs were uniformly grown on Si substrate and AFM images are shown in Fig. 1(a,b). Nanorods are highly crystalline and grown along c-axis which is reported in our previous study[36]. The schematic diagram and top view of the device are shown in Fig. 1(c,d). The sensor's performance depends on chemisorption reaction of reactive gases with adsorbed oxygen ions on ZnO NRs surface. The performance of Pd contacted ZnO NRs based sensor may be influenced by gas type, concentrations and operating temperatures. The sensor's relative response has been studied for various gases such as H_2, CH_4, H_2S and CO_2 at different concentrations and operating temperatures. Figure 2 shows sensor's relative response curve with time for 7 ppm, 12 ppm, 55 ppm, 110 ppm, 500 ppm, 1000 ppm and 10,000 ppm (1%) concentrations of gases (a) H_2, (b) CH_4, (c) H_2S and (d) CO_2 at operating

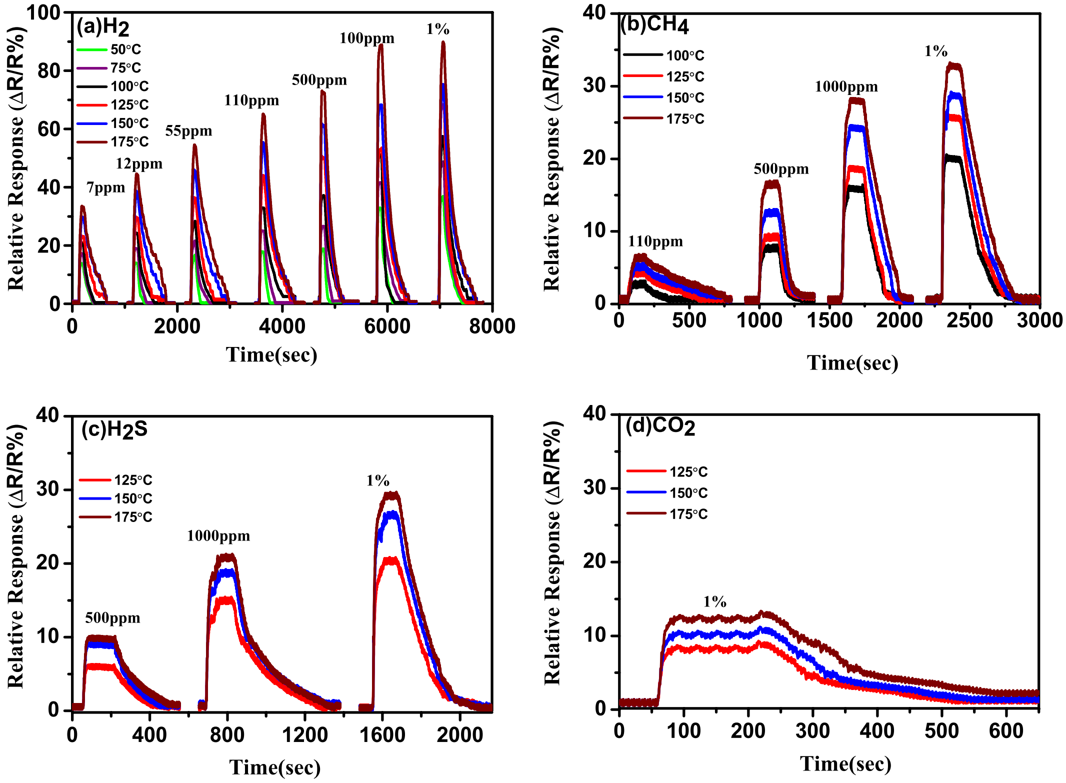

Figure 2. Sensor's relative response curve with time for 7 ppm to 10,000 ppm of gases: (**a**) H_2, (**b**) CH_4, (**c**) H_2S and (**d**) CO_2, at operating temperature ranging from 50 °C to 175 °C.

temperature ranging from 50 °C to 175 °C. The response of the sensor increases with hydrogen concentration and temperature. It was found that the sensor is able to detect very low hydrogen concentration of ~7 ppm and at low temperature (50 °C). The relative response was measured 13.86% at 50 °C and 38.47% at 175 °C. The change in relative response increases with operating temperature due to creating more chemisorbed oxygen ions on the ZnO NRs surface which further enhances desorption of oxygen. The sensor response increases from 13.86% to 37.13% with concentration from 7 to 10,000 ppm and operating temperature 50 °C. A large variation in sensor's response is observed with low concentration below 1000 ppm since hydrogen molecules react with adsorbed oxygen ions and decrease the depletion region as well as reduce the barrier height at Pd/ZnO junction. Above 1000 ppm of hydrogen chemisorbed reaction is almost saturated on ZnO NRs which is shown by very less increase in sensor's response from 86.39% to 91.26% at 175 °C of operating temperature. To study the selectivity the relative response of the device was measured for various gases such as CH_4, H_2S and CO_2 with different concentration from 7 ppm to 1%. Figure 2b shows relative response curve with time of CH_4 gas and minimum detection limit was found 110 ppm at 100 °C. During loading/deloading of the gas, methane gas molecules react with adsorbed oxygen ions on ZnO NRs surface and show decrease/increase of ZnO NRs resistance, which is similar to hydrogen gas behaviour. Although CH_4 gas is highly stable below 100 °C and with increasing operating temperature above this limit, C-H bonds starts breaking and it gives more H atoms to react with adsorbed oxygen ions and decreases sensor's resistance. Furthermore, the relative response of H_2S gas is shown in Fig. 2c and minimum detection limit was observed 500 ppm at 125 °C and maximum relative response is around 30% for 1%. This indicates less reactivity of H_2S molecules with adsorbed oxygen in comparison to hydrogen and methane gases. Sensor's relative response was also measured with CO_2 gas and shown in Fig. 2d. The minimum concentration was detected 1% at 125 °C, because of its highest stable nature in comparison to other reactive gases. Hence, the sensor shows high relative response as well as high selectivity for hydrogen gas in comparison to other gases. Sensor's relative response variation with operating temperature and concentration is shown in Fig. 3 for (a) H_2, (b) CH_4, (c) H_2S and (d) CO_2. Figure 4(a–c) depicts hysteresis studies for H_2, CH_4 and H_2S at 150 °C for increasing and decreasing gas concentrations. A stable behaviour of the sensors has been observed for each target gas.

Discussion

Gas sensing mechanism is basically surface phenomenon. The fast adsorption-desorption cycle of chemisorbed oxygen on the surface of ZnO nanorods is highly desirable to make excellent gas sensor. Thus surface sensing properties for various gases could be understood by activation energy phenomenon. The rate of resistance changes with respect to temperature for particular target gas may be assumed by Arrhenius equation which can be expressed as[37]:

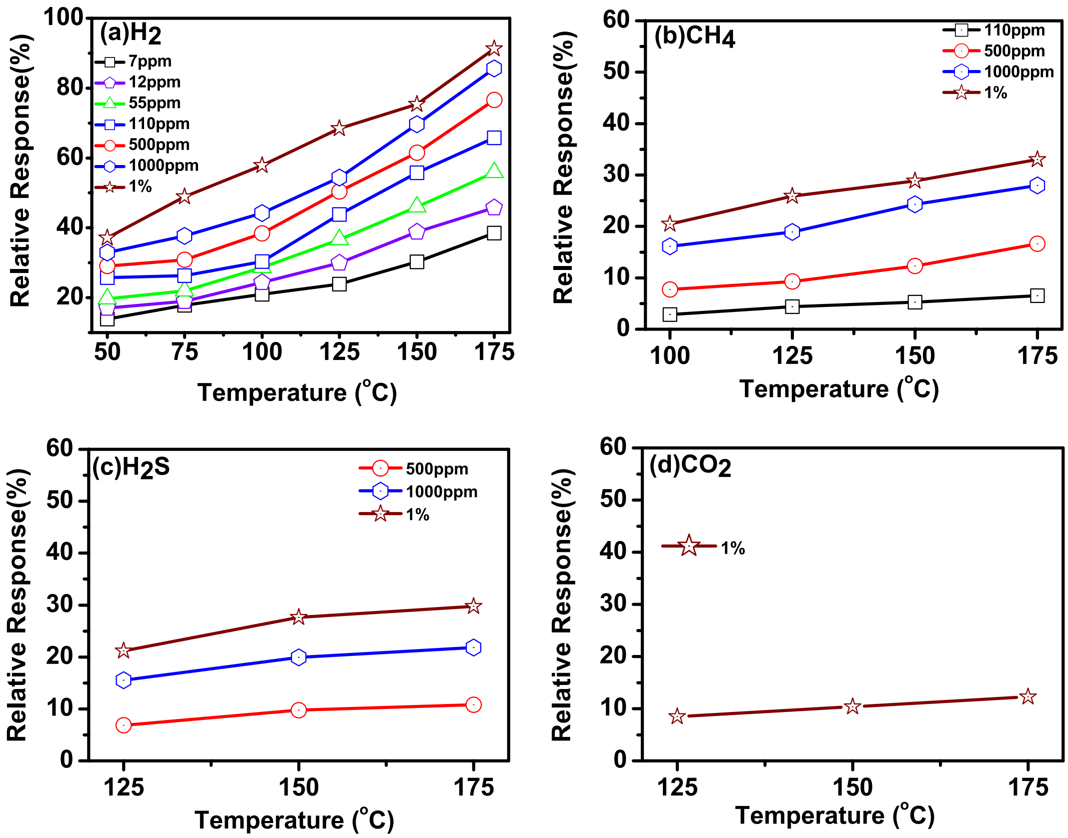

Figure 3. Sensor's relative response variation with operating temperature and gas concentration.

$$R = R_o \exp\left(\frac{\Delta E}{KT}\right) \tag{1}$$

where R is resistance of the sensor, K is the Boltzmann constant, T is absolute temperature and ΔE is the activation energy. For activation energy calculation, firstly the rate of change in resistances were evaluated from resistance verses time curves on exposure of (a) H_2, (b) CH_4, (c) H_2S and (d) CO_2 gases with 1% concentration at different operating temperature and shown in Fig. 5(a–d). It can be seen that the resistance of the sensor is decreased drastically with increase in temperature for hydrogen gas as compared to the other reactive gases. Arrhenius Plot of rate of resistance change with temperature after exposer of 1% concentration of (a) H_2, (b) CH_4, (c) H_2S and (d) CO_2 gases are shown in Fig. 6(a–d). The activation energy has been evaluated from slope of Arrhenius plot which is basically linear fitting of resistance rate with respect to temperature. The activation energy was calculated as 3.658 kJ/mol, 10.983 kJ/mol, 13.556 kJ/mol and 15.718 kJ/mol for H_2, CH_4, H_2S and CO_2 gas, respectively. The activation energy is lowest for hydrogen gas as compared to other reactive gases. Our calculated activation energy of Pd contacted ZnO NRs is smaller as compared to Wang *et al.* reported 11.8 kJ/mol for hydrogen sensor based on cluster of Pd/multiple ZnO nanorods[38]. The selectivity histogram of the sensor is shown in Fig. 7 for different concentration at 175 °C operating temperature. The sensor is able to detect minimum 7 ppm hydrogen concentration with ~38.47% relative response at 50 °C. However, for other gases minimum gas concentration sensing limits is quite high in comparison to hydrogen gas. As we know that hydrogen is smallest molecule with lowest activation energy which enhances surface reaction and corresponds to large change in depletion region of ZnO NRs. The minimum detected concentration for CH_4 gas was observed 110 ppm with 6.5% sensor response which is 10.11 times less than hydrogen gas response (~65.75). H_2S gas has quite high activation energy (13.556 kJ/mol) in comparison to both Hydrogen and methane gas, shows minimum sensing concentration to 500 ppm with relatively low sensor response ~10.82%. These sensor response is around 7 times less than hydrogen response (~76.56%) for 500 ppm concentration. CO_2 is highly stable gas with highest activation energy which makes it least reactive gas in comparison to other gases. For CO_2, minimum gas detection limit was 1% with sensor response ~12.29% which is 7.42 times less than hydrogen response (~91.26%). Cross selectivity has been calculated for Pd/ZnO nanorods based sensor to acquire more clarity for better selectivity. Figure 8 depicts cross selectivity response curve for various gases mixture (500 ppm H_2, 500 ppm H_2 + 500 ppm CH_4 and 500 ppm H_2 + 500 ppm CH_4 + 500 ppm H_2S) at 150 °C operating temperature. It is found that mixing H_2 gas with other gases with same concentration, there is slight increase in sensor's response in comparison to pure hydrogen gas. This result implies that Pd/ZnO nanorods based sensor shows high selectivity towards hydrogen gas.

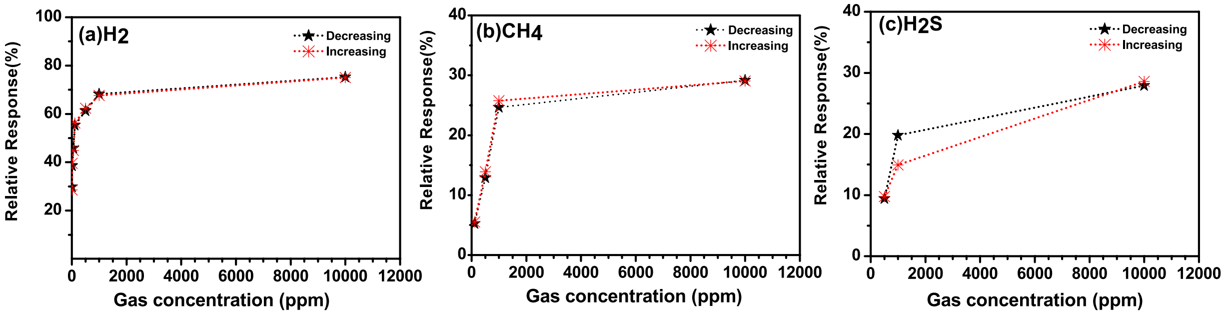

Figure 4. (**a–c**) Hysteresis studies for H_2, CH_4 and H_2S at 150 °C for increasing and decreasing gases concentration.

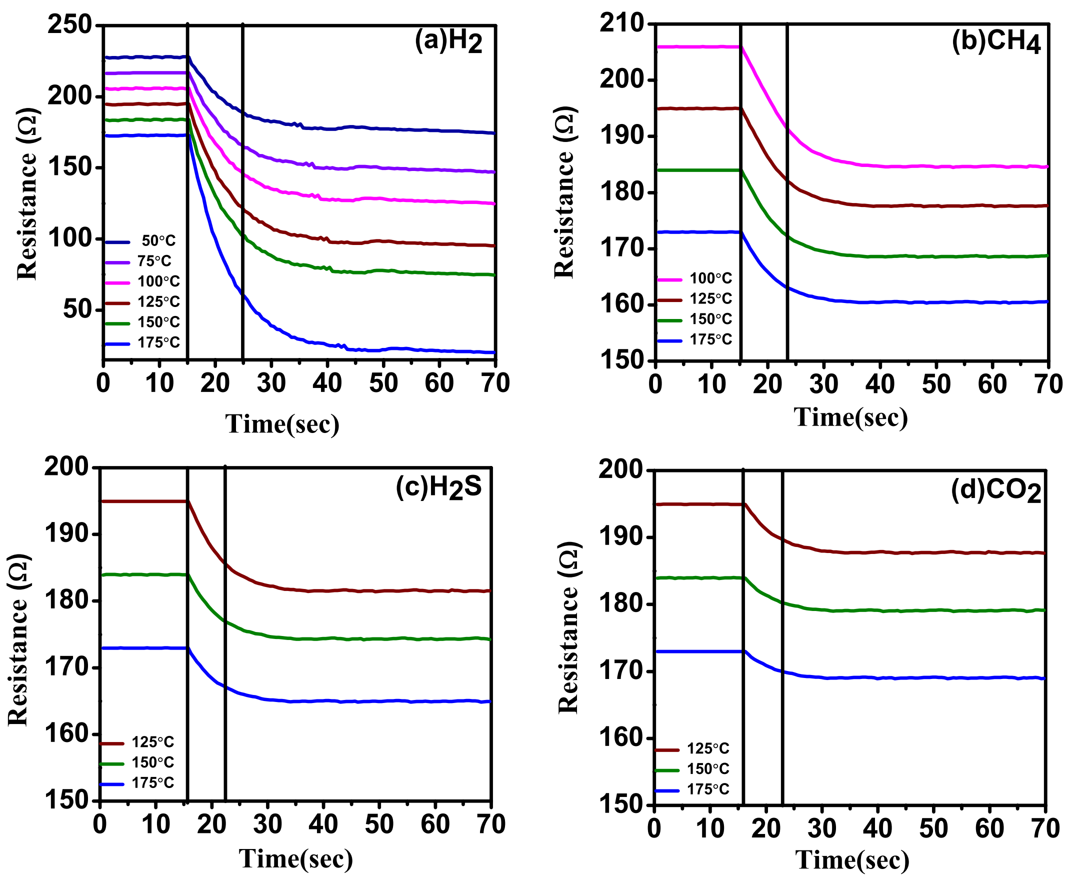

Figure 5. Resistance verses time curve for (**a**) H_2, (**b**) CH_4, (**c**) H_2S and (**d**) CO_2 gases with 1% concentration at various temperatures.

Gas sensing mechanism. Based on experimental investigation a gas sensing mechanism is proposed and shown in Fig. 9. From the figure, the relative change in depletion region of ZnO can be seen in presence of (a) Air, (b) H_2, (c) CH_4, (d) H_2S and (e) CO_2. The sensing mechanism is mainly influenced by activation energy of target gases on the surface of ZnO nanorods and a change in barrier height between Pd and ZnO NRs. When sensor chamber is loaded with target gas, these target gas molecule reacts with adsorbed oxygen ions. By removing chemisorbed oxygen ions from ZnO nanorods surface, trapped electron moves back to conduction region and decreases depletion region width of ZnO nanorods to a large extent[39–41] as shown in Fig. 9(b–e). For n-type semiconductor materials, CO_2 gas molecules also react with adsorbed oxygen ions and returns excess electrons to material. These reactions causes decreased sensor's resistance while loading of CO_2 gas[42]. Due to increasing activation energy of CH_4, H_2S and CO_2 gases in comparison to H_2, maximum sensor response is observed for hydrogen at even ppm level with maximum change in depletion region. As activation energy of target gases increases, sensor response decreases with relatively small change in depletion region. These results clearly depict gas sensing mechanism schematic in Fig. 9(b–e). Along with activation energy, operating temperature and target gas concentration also plays an important role in sensor's response. With increasing temperature, chemisorption

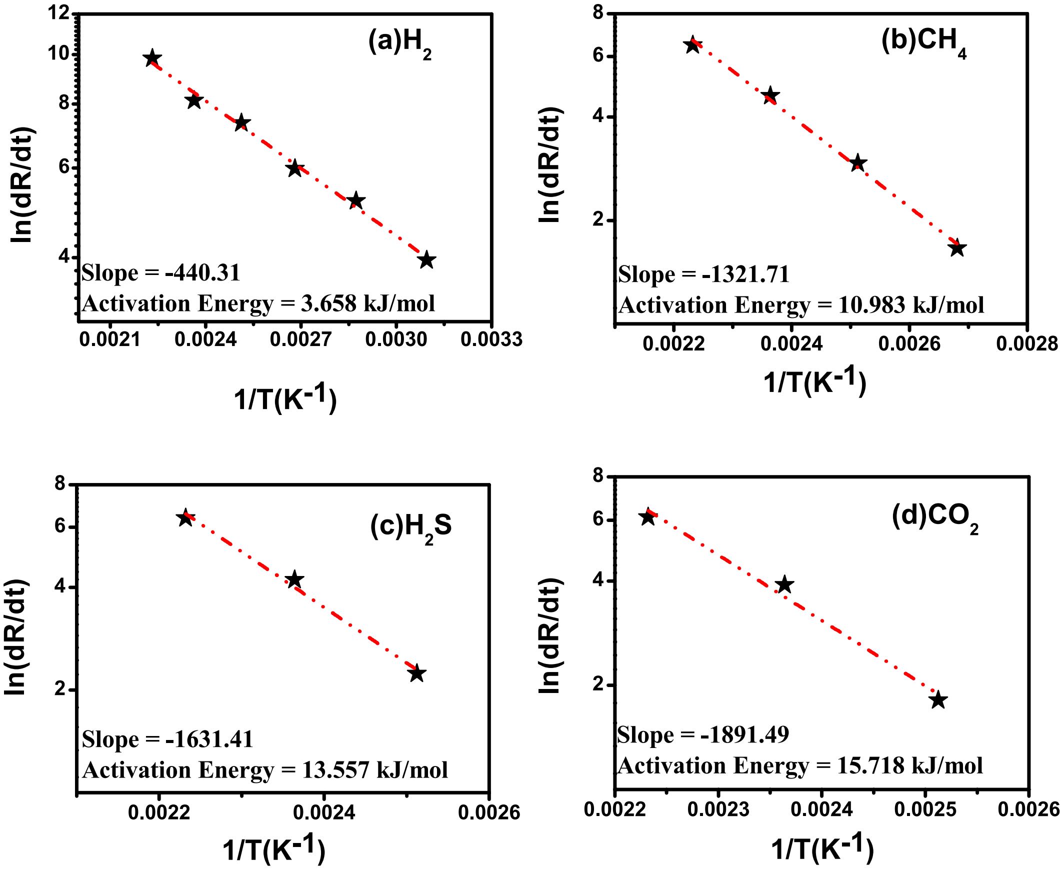

Figure 6. Arrhenius plot of rate of resistance change with temperature after exposure of 1% concentration of (**a**) H_2, (**b**) CH_4, (**c**) H_2S and (**d**) CO_2 gases.

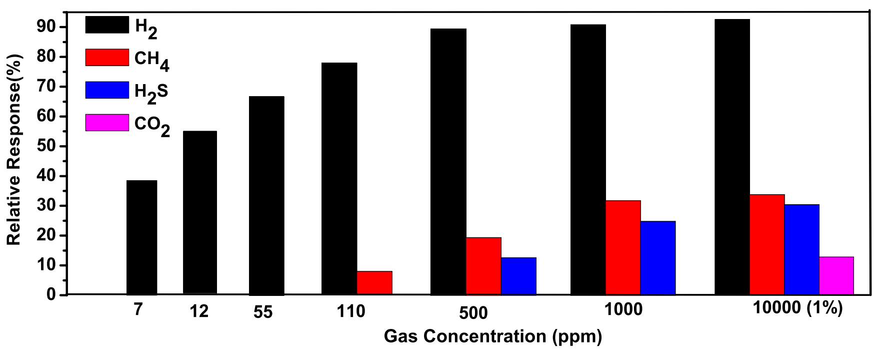

Figure 7. The selectivity histogram of the sensor to H_2, CH_4, H_2S and CO_2 at 175 °C operating temperature.

of oxygen ions on ZnO nanorods surface increases as conduction band electron get sufficient energy to overcome barrier. Due to these enhanced chemisorbed oxygen ions, there is large change in depletion region as well as in sensors resistance. While loading with target gases, it enhances desorption of oxygen ions due to which relative change in sensor resistance increases. With increasing gas concentration, it provides large reaction with adsorbed oxygen ions which further enhances sensor's response.

In case of hydrogen, the dissociation of the molecules over the Pd contact is faster and diffuse the hydrogen atom to the interface due to smallest molecular size[23,43]. Moreover, the conduction of ZnO nanorods is correlated with cross section and given as follow[44],

$$G = \frac{1}{R} = \frac{A}{\rho l} = \frac{ne\mu A}{l} \tag{2}$$

where G, n, e, l, and μ are electrical conductivity, electron concentration, length of NR and electron mobility, respectively. Fast oxygen desorption will take place when ZnO NRs are exposed to hydrogen and increase the

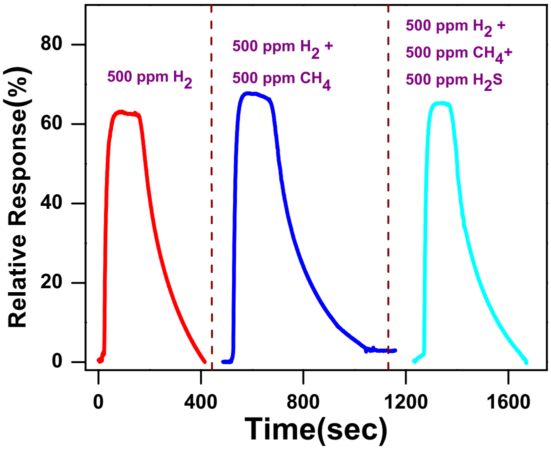

Figure 8. Cross selectivity response curve for various gases mixture (500 ppm H_2, 500 ppm H_2 + 500 ppm CH_4 and 500 ppm H_2 + 500 ppm CH_4 + 500 ppm H_2S) at 150 °C operating temperature.

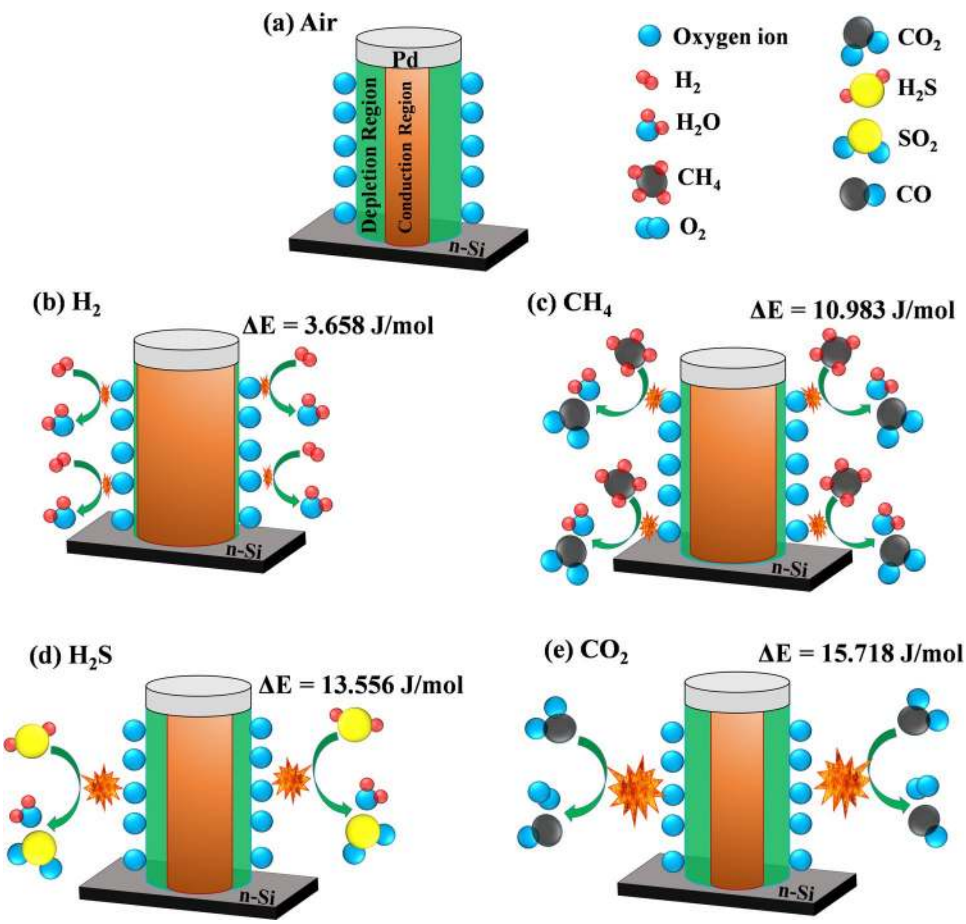

Figure 9. The gas sensing mechanism for sensor; a relative change in depletion region of ZnO NRs in presence of (**a**) Air, (**b**) H_2, (**c**) CH_4, (**d**) H_2S and (**e**) CO_2 gases.

conduction cross section channel area. When Pd is exposed to hydrogen gas, hydrogen molecule gets diffused into Pd which reduces Schottky barrier to a large extent. Because of Schottky barrier reduction along with depletion region reduction, the combine effect maximizes sensors response and makes ppm level detection possible. However as compared with hydrogen molecules, other target gases such as CH_4 and H_2S gases are less reactive to Pd contact and slower diffusion due to larger molecular weight and size. Because of these factors, there is a less change in Schottky barrier reduction which causes lesser sensor response in comparisons to hydrogen gas. While relative response of CO_2 gas is lowest occurred by the (i) more activation energy is required to break double bond than single bond (ii) highest molecular weight as compared to H_2, CH_4 and H_2S and (iii) highest activation energy of CO_2 gas provides the small relative response.

Conclusion

We have demonstrated Pd contacted ZnO NRs based sensor which shows high sensor sensitivity and selectivity for hydrogen. The sensor was analysed for selectivity test towards H_2, CH_4, H_2S and CO_2 and found best suited for H_2 even at extreme low concentration (~7 ppm) and low operating temperature 50 °C. Because of lowest activation energy ~3.658 kJ/mol of hydrogen in comparison to other reactive gases, it leads to maximum change in conduction cross section area of ZnO NRs which could be possible cause for excellent sensor's performance. A poor sensitivity was detected for CH_4 at 110 ppm (~6.5% response) which is 10.11 times less than H_2 (~65.75% response), for H_2S gas at 500 ppm (~10.82% response) which is 7 times less than H_2 (~76.56% response) and for CO_2 at 1% (~12.29% response) and marked 7.42 times less than H_2 (~91.26%). The gas sensing mechanism for Pd contacted ZnO NRs based sensor was also proposed which mainly attributed to activation energy of reactive gases. The proposed sensor is not only highly hydrogen selective but also can operate at low temperature which reduces the power consumption and prove to be energy efficient in its class.

Experimental Techniques

Vertically aligned ZnO NRs were fabricated on n-Si substrate using RF sputtering. Substrate temperature was kept constant at 600 °C during the deposition and other parameters can be found elsewhere[36]. Uniform distribution of ZnO NRs was confirmed by using AFM (Park XE-70) and FESEM techniques. For sensor fabrication, circular palladium (Pd) electrodes of 500 μm diameter were deposited on ZnO NRs with the help of DC Sputtering technique where shadow mask was used. Thickness of Pd electrodes was kept around 150 nm and 500 μm inter-electrode spacing. Gas sensing characterization was carried out in a stainless steel sensing chamber. The chamber was evacuated down to 3×10^{-3} mbar using a rotary pump. The testing gases were mixed with argon and introduced in the sensing chamber by injecting a pre-calibrated volume of target gas through mixing chamber and a gas tight syringe (Hamilton). Operating temperature was tuned from 50 °C to 175 °C. The sensor's response was measured by Semiconductor Parameter analyser (Keithey 4200-SCS) by applying a constant voltage of 1 V.

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Author Contributions

Mohit K. and V.S.B. characterized gas sensing properties, analysed data and wrote the manuscript. S.R. deposited and characterized ZnO NRs and reviewed the paper. J.S. fabricated Pd contacts and gives valuable suggestion for sensing characterization. Mahesh K. provided continuous supervision during research work and thoroughly reviewed the manuscript.

Additional Information

Competing Interests: The authors declare that they have no competing interests.

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