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# Fabrication and Characterization of ZnO Single Nanowire-Based Hydrogen Sensor

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Vertically aligned ZnO nanowires were grown on *c*-plane sapphire substrate by metal organic chemical vapor deposition technique. The nanowires were single crystalline and structurally uniform and did not exhibit any noticeable defects. Pt/ZnO single nanowire Schottky diodes were fabricated by using e-beam lithography and then characterized by measuring temperature-dependent I−V characteristics. The diode exhibited a low Schottky barrier height of 0.42 V and ideality factor of 1.6 at room temperature. Temperature-dependent hydrogen-sensing measurements were carried out with different hydrogen concentrations. A good sensing characteristic ($S \approx 90\%$) has been observed at room temperature with a response time of ~55 s.

## 1. Introduction

Hydrogen ($H_2$) is a potential source of energy, which may replace the present fossil-based transportation fuels. It is also used as an important reagent in chemical industries. However, it is highly explosive above 4 vol % because of its low flash point (−253 °C).[1] Therefore, $H_2$ leakage detection at an early stage is not only necessary but essential for safety. Solid-state $H_2$ sensors based on pure Pt, Pd, or Pd-containing alloys have been thoroughly explored because the interaction with $H_2$ decreases the work function and increases the resistance compared to pure material.[2] Several other materials ($SnO_2$, $InO_3$, $WO_3$, and CNT) are currently being investigated for the active materials of sensors.[3,4] However, a high operation temperature is generally required for the better performance of the above-mentioned sensors. Recently, many investigations have been carried out on the exploration of selective materials to make the sensor more sensitive and reliable. In this concern, tremendous attention has been focused on ZnO as a gas sensing material because of its high mobility of conduction electrons and good chemical and thermal stability under the operating conditions of the sensors.[4−6] In addition, single crystalline nature, high mechanical strength, high temperature stability in oxygen ambient, and ease of fabrication on several substrates by various techniques[7−9] are other advantages of ZnO nanostructures.

Single nanowire-based sensors are of particular interest because they can be fabricated by using conventional lithography technique. In addition to low cost and great miniaturization potential, the large surface-to-volume ratio and nanoscale dimension allow quick diffusion of gases into and from the nanostructure. Thus, the rate of reaction increases, which leads to a higher sensitivity with faster response and recovery time. Nanoscale sensors also often provide a lower limit of detection because of a larger change in their electronic properties upon surface adsorption.

In the case of ZnO nanostructure-based $H_2$ sensor, the surface of the nanostructures plays a vital role. In that case, the contacts at the two ends are mostly chosen to be ohmic in order to enhance the change in conductance due to surface effect of the nanostructures. The surface-adsorbed gas molecules modify the electronic surface states and vary the electron concentration which is responsible for the change in conductivity of nanosensors.[10] At room temperature, electrons released because of gas exposure are much fewer as compared to the electron concentration in nanowire. Therefore, the relative change of conductance before and after gas exposure is small. Because the interaction energy of chemisorbed oxygen atom is large (1−10 eV), metal-oxide gas sensors generally require high operating temperature (above 100 °C) to overcome the energy limits and achieve high sensitivity.[11] However, the high operating temperature adversely affects the sensor's reliability and durability and makes the sensor expensive with many complicated heating elements.

In order to improve the sensitivity at room temperature, we deliberately introduce a nonsymmetrical Schottky contact at one end of a ZnO single nanowire-based nanodevice. Here, the surface depletion layer controls the density and mobility of electrons in the nanowire, whereas the contact barrier controls the transport of electrons between the nanowire and the electrode. Because the width of the surface depletion is significantly smaller than the diameter of the nanowire, the surface depletion has little influence on the density and mobility of the electrons in the nanowire. However, the change in potential barrier at the Schottky contact greatly modifies the current conduction. The presence of impurities, inconsistencies, and asymmetry in the structure may alter the effective potential barrier and inhibit the flow of charge carriers, which may change the device characteristics. To solve this problem, defect-free nanowires are required. In this communication, we have studied $H_2$-sensing properties of Pt/ZnO nanowire Schottky diodes by measuring current−voltage ($I-V$) relationships at different temperatures.

## 2. Experimental Details

ZnO nanowires were synthesized on *c*-plane sapphire by metal organic chemical vapor deposition method. Diethyl zinc and high-purity oxygen were used as the Zn and O sources, respectively. The ZnO nanowires were then dispersed on Si substrates with 500 nm of $SiO_2$ layer. Prior to dispersion of nanowires, preassigned gold micropads were fabricated on the substrate by using photolithography and lift-off techniques. To

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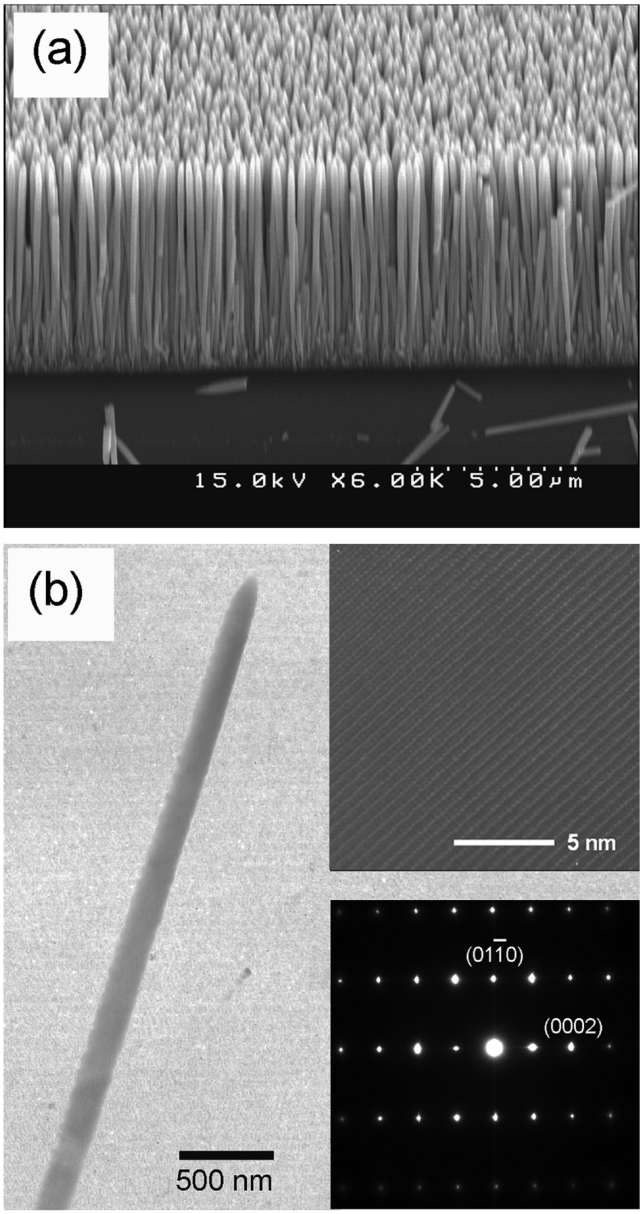


**Figure 1.** (a) FESEM, (b) bright field TEM images of ZnO nanowires grown on *c*-plane sapphire. The inset of panel b shows the corresponding HRTEM and SAED pattern.

form the ohmic contact with ZnO nanowire, 100 nm of Ti and 200 nm of Au were successively deposited on one side via standard e-beam lithography and sputtering of metals followed by rapid thermal annealing at 550 °C for 1 min in $N_2$ atmosphere. In order to fabricate Schottky diode, Pt was deposited at another end of the nanowire. The surface morphology of as-deposited ZnO nanowires and single nanowire-based Schottky diodes was analyzed by field-emission scanning electron microscopy (FESEM). In addition, the microstructure of ZnO nanowires was observed by using high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F). Temperature-dependent (300−550 K) $I-V$ measurements were performed by using a HP4145B semiconductor parameter analyzer. The sensitivity tests were carried out in a test chamber, where the change in current was measured at a fixed forward voltage (4 V) because of gas exposure. A known amount of highly purified $H_2$ was injected from an ampule along with argon gas acting as a diluting agent to get the required percentage (in

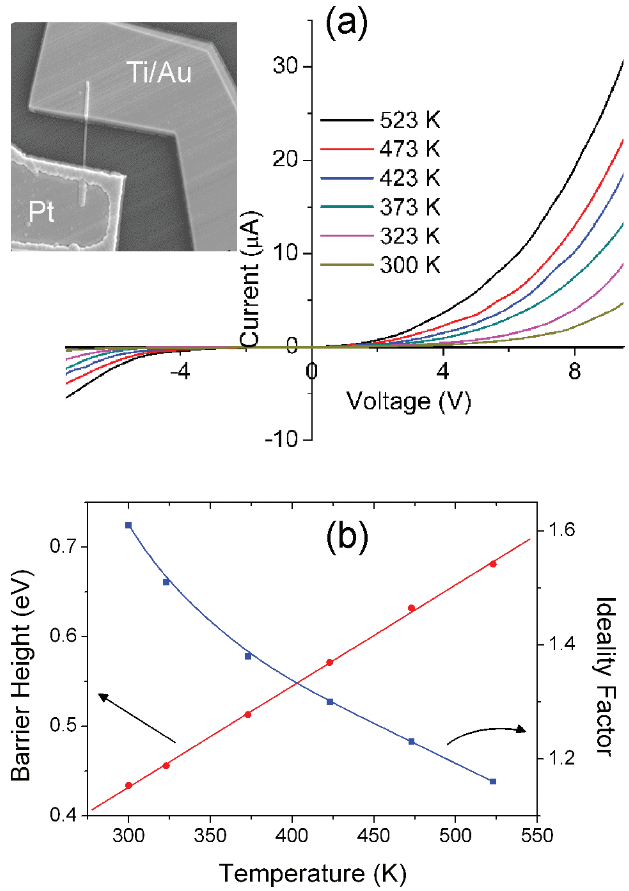


**Figure 2.** (a) Temperature dependent $I-V$ characteristics for a representative Pt/ZnO nanowire Schottky diode before gas exposure. The inset shows the SEM image of a single nanowire Schottky diode. (b) Variation of barrier height ($\Phi_B$) and ideality factor ($n$) with temperature (in kelvins) for Pt/ZnO nanowire Schottky diode.

ppm) of $H_2$ in the measuring chamber. The sensing characteristics were then recorded at different temperatures with various $H_2$ concentrations.

## 3. Results and Discussion

Figure 1a shows a typical FESEM image of vertically aligned ZnO nanowires (diameter ≈ 200 nm) grown on *c*-plane sapphire substrate. The appearance of a prominent (0002) peak in XRD pattern (not shown here) confirms the crystalline nature of ZnO nanowires. Figure 1b shows the bright field TEM image of a ZnO nanowire. The diameter of the nanowire is around 200 nm and uniform through out its length. In order to further investigate the structural characteristics of ZnO nanowire, a HRTEM experiment was carried out, and the magnified image is shown in the inset of Figure 1b. HRTEM images at different parts of the nanowire indicate that the nanowire is structurally uniform and free from any noticeable defects. Furthermore, the HRTEM image has confirmed that the single crystalline ZnO nanowire is preferentially oriented along the *c*-axis direction with a lattice spacing of 0.52 nm. The selective area electron diffraction (SAED) pattern (inset of Figure 1b) also shows that the nanowire exhibits a single crystalline nature. These results are almost consistent with the FESEM observation.

SEM image of single ZnO nanowire device with an electrode gap of 2.5 $\mu$m is shown in the inset of Figure 2a. Current will flow through the nanowire device upon applying a potential across the electrodes. Temperature-dependent $I-V$ plots for a representative Pt/ZnO nanowire Schottky diode before $H_2$

exposure are shown in Figure 2a. In general, the primary conduction mechanism in Schottky diode is attributed to the flow of majority charge carriers over the barrier by a thermionic process. Depending on the temperature ($T$) and applied voltage ($V$), different transport mechanisms might be simultaneously operative in the Schottky diode and modulate the charge transport. Assuming that the themionic emission is the most predominant mechanism, the general form of the temperature dependence of the current may be expressed as[12,13]

$$I = AA^{*} \exp(-\beta\Phi_{B}) \exp\left[\frac{\beta(V - IR)}{n}\right] \tag{1}$$

where $\Phi_B$ is the effective barrier height, $A$ is the junction area, $A^*$ is the Richardson constant, $n$ is the ideality factor, $R$ is the series resistance, and $\beta = q/kT$. Thus, the electrical characterization of a Schottky diode necessitates the determination of the barrier height and the ideality factor. For an ideal diode, the diode ideality factor should be nearly equal to unity. But in a real situation, it may increase when the effects of series resistance, leakage current, and so forth come into play. In such a case, the generalized Norde method could be used to evaluate the effective barrier height and diode ideality factor from $I-V$ measurements.[13] The effective barrier height and ideality factor measured at different temperatures for Pt/ZnO nanowire Schottky diode are shown in Figure 2b. The barrier height can be seen to increase linearly with temperature. On the other hand, the ideality factor for the Schottky diode decreases from 1.62 to 1.15 with an increase in temperature. Deviation of the ideality factor from unity may be due to the existence of high series resistance.

The sensitivity is defined as[13]

$$S = \frac{I_{G} - I_{Ar}}{I_{Ar}} \tag{2}$$

where $I_G$ and $I_{Ar}$ are the currents in $H_2$ and argon ambient, respectively. The above expression can be used for both the forward and the reverse current modes at a fixed voltage. Figure 3a shows the variation of sensitivity with $H_2$ concentration at room temperature in the forward bias mode (4 V) for a representative device. One can observe that the sensitivity increases linearly with $H_2$ concentration until 2000 ppm, beyond which it increases slowly and tends to saturate. It seems that because of the increase in $H_2$ concentration, more gas molecules are available to be in contact with the device. Thus, one would expect the response to increase up to a certain limit with an increase in $H_2$ concentration as observed here. Afterward, with the increase in concentration, the sensitivity tends to saturate. This may be due to a saturation of adsorption of $H_2$ atoms at Pt/ZnO nanowire interface and lack of adsorbed oxygen ions at the nanowire surface to react with gas molecules.

Consequently, a time-resolved sensitivity measurement has also been done. Figure 3b represents the variation of sensitivity with time, measured at room temperature (300 K), when the test gas ($H_2$ at 2500 ppm) is introduced in the chamber. It is observed that the maximum sensitivity is obtained within 75 s. After removal of the test gas, the sensor tends to come back to its initial state, and this change is exponential. Sensitivity decreases fast for the first 50 s and then slowly to its original state. Figure 3c represents the same observation for the repeated cycles. The poisoning of the sensor sample is observed to be quite less even after repeated exposures. The response time is

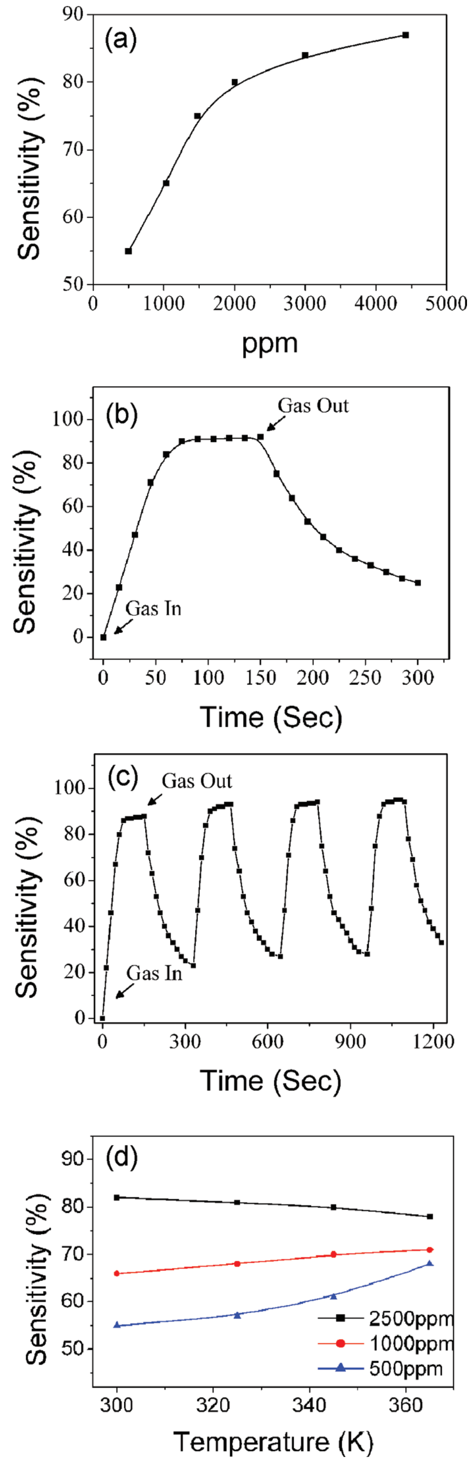


**Figure 3.** (a) Variation of sensitivity with $H_2$ concentration measured at room temperature in the forward current mode at 4 V. (b) Room-temperature response behavior for 2500 ppm of $H_2$. (c) Same as panel b for repeated cycles. (d) Temperature-dependent sensitivity for three representative $H_2$ concentrations.

defined as the time taken for the sensor to reach 90% of the saturation value after gas exposure. The above observation suggests that the response time in these devices is ~55 s. The response time for Pd/nano-GaN Schottky diode reported by Das et al.[13] was ~12 min. On the other hand, Rout et al.[14] have observed a higher response time (~300 s) by monitoring the change in conductivity due to $H_2$ exposure. Thus, the response time of the single nanowire-based Schottky diode, studied here, is superior to those reported recently by other researchers.[13,14]

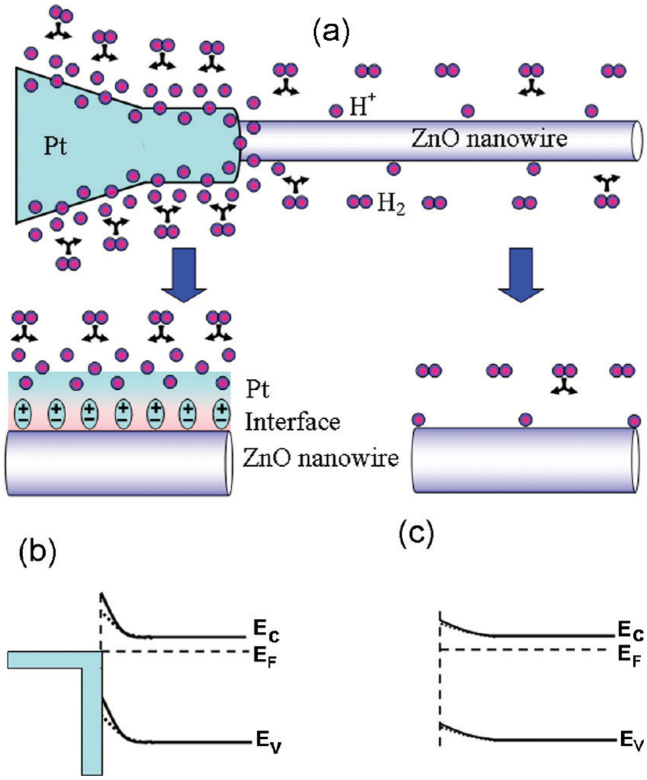


**Figure 4.** (a) Diagram of the Pt/ZnO single nanowire $H_2$-sensing mechanism. Energy-level Diagram of (b) Pt/ZnO nanowire interface and (c) ZnO nanowire surface.

The contribution of ZnO nanowire surface and Pt/ZnO nanowire Schottky junction to the sensing mechanism was varied with gas concentration and temperature. In order to investigate the detail sensing mechanism, we have measured the sensitivity at different temperatures with different gas concentrations and plotted the results in Figure 3d. The measurements, reported here, are taken at different temperatures after the same interval (60 s) of gas exposure after the equilibrium has been established. The sensitivity-versus-operating-temperature curve shows a maximum at room temperature for 2500 ppm and decreases very slowly with increasing temperature, whereas it increases slowly but linearly with temperature for $H_2$ concentration of 1000 ppm. On the other hand, for a lower $H_2$ concentration (500 ppm), the sensitivity increases slowly up to 323 K, and beyond that, appreciable change in sensitivity is observed. This can be explained by the temperature-dependent adsorption and desorption process on both the nanowire surface and the Schottky junction. Although individual contribution to the sensing mechanism is not distinguishable, a qualitative description can explain the whole mechanism by considering the change in band diagram in two different parts, namely, ZnO nanowire surface and ZnO/Pt Schottky junction.

The $H_2$-sensing mechanism, investigated in this study, is schematically shown in Figure 4. Because of the geometry of the devices, the electric field near the junction between the ZnO nanowire and the metal is much higher. As a result, the gases around the contact easily dissociate, and ionized gases get adsorbed at the ZnO/Pt Schottky junction even at room temperature. The change in Schottky barrier height is likely to be the most important for $H_2$ sensing, but the ZnO nanowire surface has also a contribution. However, this mechanism would be expected to exhibit a large dependence on the temperature and the concentration of gas around the devices.

The sensing mechanism at the nanowire surface can be explained in terms of the oxidizing/reducing gas effect. It is well-known that the ZnO surface adsorbs oxygen species ($O_2^-$, $O^{2-}$, $O^-$) from air by trapping conductive electrons and makes the nanowire more resistive. Moreover, for a ZnO nanowire, a high surface-to-volume ratio provides a large number of surface atoms, which can lead to the insufficiency of surface atomic coordination and high surface energy.[10] Therefore, the surface is highly active, which promotes further adsorption of oxygen from the atmosphere. On the other hand, when the nanowire is exposed to $H_2$ environment, the reductive gas decreases the concentration of oxygen species on the nanowire surface, which in fact increases the electron concentration in the nanowire. It should be noted that the chemisorbed oxygen species depend strongly on temperature. Upon exposure to $H_2$, it is the chemisorbed surface oxygen ions that participate in the redox reaction preferably at higher temperature.[15] The electrons, released from this process, are responsible for the change in electrical properties of ZnO nanowire through band bending. Thus, at higher temperatures, the nanowire surface will become more active for $H_2$ sensing. On the other hand, the characteristic of the nanosensor is largely determined by the behavior at the Schottky junction. The electrical response comes from the variation of the Schottky barrier height and barrier width as a result of adsorption of gaseous species at the Schottky contact. The response due to adsorption can be explained from the band diagram at the metal/nanowire contact. After the exposure to $H_2$, Pt adsorbs $H_2$ by catalytic chemical adsorption. Some of the $H_2$ atoms diffuse through the thin metal layer and form a dipole layer at the interface of the metal−semiconductor contact, which reduces the Schottky barrier height.[16] Although that may change the barrier width, it is the height of the barrier that matters significantly for charge transport at room temperature. As a result, both the forward and the reverse currents increase with the increase of the $H_2$ concentration. However, the Pt surface gradually saturates with the increase in $H_2$ concentration; therefore, the rate of change of current decreases. When the gas ambient is switched from $H_2$ to air, the oxygen reacts with $H_2$, and the resistance of the nanowires changes back to the original value. This is an attractive process for long-term application of $H_2$ sensor.

The sensitivity depends on the combined effect of operating temperature and $H_2$ concentration. The Schottky barrier height increases with temperature, whereas it decreases with an increase in $H_2$ concentration. For higher $H_2$ concentration (2500 ppm), the interface becomes saturated even at room temperature. This results in a small change (decrease) in barrier height because of further adsorption of $H_2$ atoms with temperature, but the barrier height of the junction increases. As a result, the sensitivity decreases slowly with an increase in temperature. But for low $H_2$ concentration (500 ppm), the interface does not saturate, and more $H_2$ atoms can be adsorbed with an increase in temperature. Thus, the sensitivity increases with an increase in temperature for lower $H_2$ concentration. Quick response and stability are also important characteristics of sensors. For a quick response, the electron exchange must take place rapidly so that equilibrium is established during the measurement. Because the Pt/nanowire interface is very small, a thin adsorbed $H_2$ layer is formed quickly at the interface, which may block further electron exchange, and thus, equilibrium occurs. Hence, a further increase in $H_2$ concentration may eventually saturate the Pt/nanowire interface, which limits further electron exchange. Thus, the interface of the Pt/ZnO nanowire Schottky device plays a significant role in quick response at room temperature $H_2$ sensing.

## 4. Conclusion

In summary, I−V characteristics of Pt/ZnO single nanowire Schottky diodes were studied. Depending on the temperature, the Schottky diode exhibited a good rectifying behavior with a low Schottky barrier height of 0.42−0.67 V and ideality factor of 1.6−1.2. The $H_2$-sensing behavior of the device has suggested that it has good sensing characteristic ($S \approx 90\%$) at room temperature with a response time of ~55 s. The sensitivity shows a maximum at room temperature for $H_2$ concentration of 2500 ppm and decreases very slowly with an increase in temperature, whereas it increases slowly with temperature for $H_2$ concentration of 500 ppm.

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