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An Investigation on Electrical and Hydrogen Sensing Characteristics of RF Sputtered ZnO Thin-Film with Palladium Schottky Contacts

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***Abstract*— Fabrication and characterizations of a hydrogen sensor with palladium Schottky contacts, grown on RF (Radio Frequency) sputtered zinc oxide thin film is reported. Temperature dependence performance analysis of the proposed sensor was carried out at different hydrogen concentrations (50 ppm to 1000 ppm) and temperatures (25°C-200°C) using *I-V* measurements. Lateral shifts have been observed in the Schottky diode *I-V* (current-voltage) characteristic when the device was exposed to hydrogen, and this could be attributed to the reduction of Schottky barrier height (SBH). The optimum performance of the sensor was obtained at 150°C with maximum SBH variation of 144 meV at 1000 ppm hydrogen. Transient sensor performance at optimum temperature has also been analyzed and sensitivities ranging from 224 % to 1125 % with a minimum response time of 55 seconds and recovery time of 26 seconds have been obtained. The response of sensor towards methane and nitrogen dioxide are also discussed. The basic current-voltage and capacitance-voltage characteristics of Pd/ZnO thin film are also reported, which confirmed its excellent rectifying properties. The basic microstructure studies of ZnO thin film were also investigated using X-ray diffraction (XRD), Scanning electron microscope (SEM), Atomic Force Microscopy (AFM), Energy dispersive X-Ray spectroscopy (EDX) and Photoluminescence (PL) measurements. The proposed sensor has proven to be economical, due to its high sensitivity and easy to fabricate structure with a limited number of processing steps.**

***Index Terms*— Electrical characteristics, Hydrogen sensing, Metal-semiconductor interface Palladium catalyst, Schottky diode, Zinc oxide (ZnO) thin film.**

I. Introduction

Semiconducting oxides based nano-electronic devices have got a remarkable potential for applications in the field of gas sensing. Compared to bulk devices, nanostructure-based sensors have drawn ever increasing recognition, because of their small size, better sensitivity, fast responses and large surface to volume ratio [1]-[4]. Metal oxide as sensing material is used as low-cost alternative in gas sensors and among them ZnO has became a focus of intense research, due to its distinct properties such as wide band gap (3.37 eV) large exciton binding energy (60 meV), high mobility, high chemical and thermal stability, etc. [1]-[8]. Moreover, nanostructured ZnO thin film is reported to have better surface-adsorption ability and excellent surface charge-transfer properties which make it a suitable candidate for gas sensors [9]. An interesting approach to increase the sensitivity of ZnO to target gases and to reduce the sensing temperature is the usage of noble metal catalysts like Pt or Pd in the sensing layer [1], [10]-[16]. Palladium is reported to have high hydrogen solubility and can remarkably increase hydrogen sensitivity and selectivity of the sensor [13], [14]. It is noteworthy that, ZnO thin film can form excellent Schottky diode with Pd and the presence of reducing gases like hydrogen will lead to Schottky barrier height modulation, which is accountable for hydrogen sensing [12]-[19].

Hydrogen can act as a new energy source, an alternative to fossil fuels and hence the research in hydrogen sensing has acquired great thrust, as it is a colorless, odorless and highly inflammable gas. In 1962, Seiyama *et al.* [7] reported that conductivity of ZnO thin film was responsive to reactive gases in air at an elevated temperature of 300°C and it marked the beginning of history of ZnO thin film based gas sensors. Husam *et al.* [20] reported on hydrogen gas sensing of ZnO thin film deposited using RF sputtering. Hassan *et al*. [21] and Wang *et al.* [22] studied the hydrogen sensing behavior of ZnO nanorods. Ranwa *et al.* [23] reported a sensitivity of 67% for the nanosensor based on ZnO NRs with gold circular Schottky contacts. Palladium has also undergone wide investigation as a catalyst material in gas sensing where, Ren *et al.* [24] reported on hydrogen sensitivity of ZnO wires with Pd nanoparticles and Shinde *et al.* [25] reported the effect of Pd sensitization on porous ZnO nanobeads for LPG detection. Weichsel *et al*. [26] reported the hydrogen sensor based on Pd/ZnO Schottky diode on GaAs by MOCVD. Yadav *et al.* [10] and [11] have reported the hydrogen sensitivity of Pd/ZnO Schottky diode deposited using sol-gel and thermal evaporation method at room temperature.

The main objective of the proposed work is to evaluate the steady state hydrogen sensing *I-V* and transient characteristics of the RF sputtered ZnO thin film with Pd Schottky contacts on n-silicon substrate. Hydrogen sensing characterizations of the sensor have been analyzed at a wider temperature range from 25°C to 200°C. Among the various technique of thin film deposition, we have preferred RF sputtering due to its advantages such as uniformity in thickness, high purity, better film adhesion, etc [20]. The basic microstructure studies of ZnO thin film and electrical characterization of Pd/ZnO Schottky diode are also reported.

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II. EXPERIMENTAL DETAILS

A. Device Fabrication

We have employed RF Sputtering technique for the deposition of nanocrystalline ZnO thin film on n-Si substrate (Resistivity of 1-10Ω). ZnO of 99.99% purity was equipped as the target for the deposition. Si substrate was thoroughly cleaned using standard RCA process and subsequently dipped in Hydrofluoric acid for 60 seconds to remove the native oxides. The target and substrate were loaded into the sputtering chamber of Tecport sputtering unit by maintaining the target to substrate distance at 11 cm. The chamber pressure was reduced to 1.5×10^{-6} Torr and RF power of 100 W was used to create the plasma. Argon with 99.999% purity was used as the sputtering gas, and its concentration was kept at 15 SCCM (standard cubic centimeter per minute). Further, ZnO was sputter deposited on Silicon substrate at the deposition pressure of 1.8×10^{-2} Torr for 40 minutes. The as-deposited ZnO thin film was undergone rapid thermal annealing at 450°C for 10 minutes in a nitrogen atmosphere, to improve the crystalline nature of the film. The film thickness was measured by the surface profiler and was obtained around 200nm**.**

The sensor structure (Pd-ZnO) considered in this study was obtained by depositing Pd circular Schottky contacts on annealed ZnO thin film through RF sputtering technique with the help of a shadow mask, which had closely packed pores. An array of Pd contacts, each of area 3.84×10^{-3} cm^{-2}, and thickness 80 nm were formed on ZnO thin film surface by taking care of the fact that enough ZnO surface remain uncovered to facilitate the oxygen adsorption, which is supposed to be the crucial step towards gas sensing mechanism. Ohmic contacts were realized by E-Beam Evaporation of Al metal of thickness 80 nm on the back side of Silicon substrate. Further, the device was undergone rapid thermal annealing at 450°C for 5 minutes, to enhance the quality of metal contacts.

B. Characterization

The crystalline orientations and crystallinity of the ZnO thin films were recorded by X-ray diffraction (XRD) with an 18-kW Cu rotating-anode-based X-ray diffractometer (Panalytical X-Pert Pro) in the range of 20°-80°. Field emission scanning electron microscope (Nova Nano FE-SEM, 450) and Atomic force microscope (Bruker, Multimode 8) were used to analyze the surface morphologies, grain structure, and surface roughness of the thin film. Photoluminescence (PL) measurements at room temperatures were carried out using fluorescence spectrometer (Perkin Elmer, LS55) which used a high energy pulsed Xenon source for excitation.

C. Gas Sensing Measurement Set-up

The gas sensing characteristics of the device were recorded using a computer controlled gas sensing set-up comprises of a static mixer, mass flow controller (MFC), Keithley 237 source measure unit, a heater made of halogen bulb covered by graphite and a data acquisition system. The target gas of desired concentration was obtained by mixing synthetic air and the target gas (hydrogen) using a static mixer, and the total flow was maintained at 500 standard cubic centimeters per minute (sccm) using computer controlled MFC. A Matlab program was used to control the gas flow cycles and record target gas concentration and sensor current. The sample was exposed to target gas pulses of varying concentration in synthetic air carrier gas.

III. STRUCTURAL AND ELECTRICAL CHARACTERISTICS

The Fig. 1(a) shows the XRD pattern of RF sputtered ZnO thin film. All the peaks are in accordance with the standard values of JCPDS card no.36-1451, which confirms the formation of (002) axis oriented ZnO thin film with all the diffraction peaks indexed to that of Wurtzite structure [3]. It is worth stating that, ZnO is a potential material for gas sensing application owing to its wurtzite open structure, with empty Octahedral sites, providing plenty of gas adsorbing sites [27], [28]. The particle size was calculated to be around 18 nm from XRD data using Scherrer's formula, which also indicates the high surface to volume ratio of the film [3].

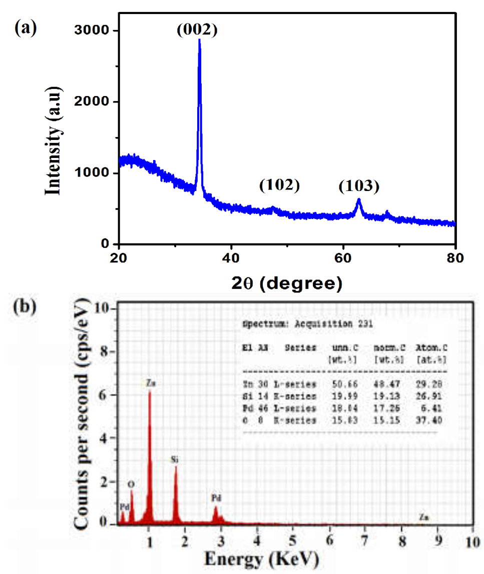

Fig.1. (a) XRD spectra of ZnO thin film on Si substrate (b) EDX spectrum of Pd/ZnO/Si, inset shows the constitution of various elements in the sample.

Fig. 1(b) elucidates the EDX spectrum of the proposed sensor which confirms the deposition of Pd over ZnO thin film grown on Si substrate. Surface roughness is an important factor which influences the gas sensing capability of the film, since it will increase the number of gas adsorbing sites [14]. The surface morphological characteristics of the ZnO thin film was studied using FE-SEM and the corresponding image is depicted as the inset of Fig.2(a) that shows randomly oriented grains. It confirms the high surface to volume ratio of the film which can greatly favor the sensor response by providing a large number of gas adsorbing sites. The atomic force microscopy image illustrated in Fig. 2(b) confirms that the deposited film has got a considerably rough surface with roughness (R_{max}) of 24.4 nm and can be considered ideal for the gas sensing purpose. Fig. 3 depicts the photoluminescence spectra of ZnO thin film procured in the wavelength range of 200-800nm at room temperature. The film shows a strong UV

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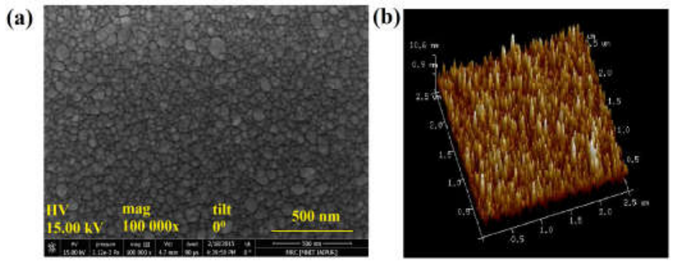

Fig . 2 (a). FE-SEM image of ZnO thin film on Si substrate. (b) AFM image of ZnO thin film on Si substrate

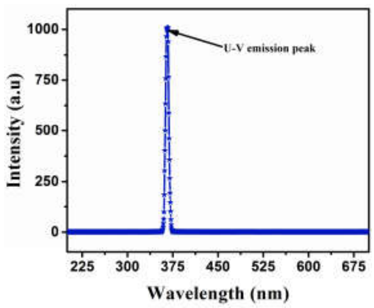

Fig.3. PL spectrum of RF-Sputtered ZnO thin film.

emission peak at 365nm (near band edge emission), indicating good crystallinity of the film and it is credited to the existence of free exciton recombination [1], [3].

Fig. 4 demonstrates the *ln I-V* characteristics of the Pd/ZnO Schottky diode at room temperature, whereas its inset provides the I-V characteristics and the schematic representation of proposed device. It confirms the excellent rectifying property of the diode with the high rectifying ratio (Ratio of diode current at +4V to current at -4V) of 2272 at an external bias of ±4V. Since the Al/ZnO/Si/Al junction has an ohmic characteristic which was reported elsewhere [1], the proposed structure behaves as vertical Pd/ZnO Schottky diode as reported by others [29], [30]. We have measured *I-V* characteristics of about five Schottky diodes in the array, and all of them provided almost same characteristics. Assuming, thermionic emission as the current transport mechanism of Pd/ZnO Schottky junction, its *I-V* characteristics is given by (1) for the applied bias of $V > \frac{3kT}{q}$

$$I \approx I_0[\exp(\frac{qV}{\eta kT}) - 1] \quad (1)$$

Where,

$$I_0 = AA^* T^2 \exp(\frac{-q\phi_b}{kT}) \quad (2)$$

I_0 is the saturation current, q is the electronic charge, ϕ_b is the effective barrier height at zero bias, V is the applied voltage, A is the diode area, A^* (32cm^{-2} K^{-2}) is the Richardson constant, k is the Boltzmann constant and η is the ideality factor [31], [32]. The ideality factor, η is calculated from the slope of the linear region of ln I-V characteristics [27] given in Fig. 4 using (3) and is obtained as 3.48.

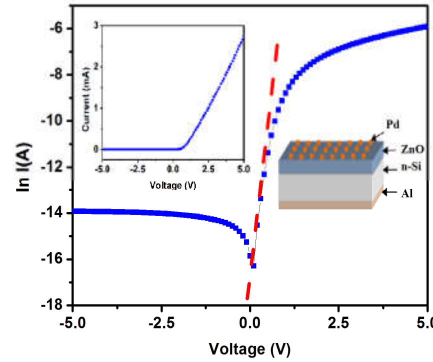

Fig.4. ln I-V characteristic of Pd/ZnO Schottky junction at room temperature. The inset shows I-V characteristics and schematic representation of proposed sensor.

$$\eta = \frac{q}{kT}\frac{dV}{d\ln(I)} \quad (3)$$

The other empiric parameters of Schottky diodes such as saturation current, effective barrier height were calculated according to the standard method, using equations (1) and (2) [1], [31], [32] and obtained the values as 9.14x10^{-8} and 0.68 eV respectively. These values are in good congruence with the results reported by other researchers [29], [30]. The non-ideal values of ideality factor and barrier height suggests the existence of different current conduction mechanisms other than thermionic emission in the Schottky junction like tunneling, tunneling-recombination, field emission, etc., the presence of interface states, Fermi energy level pinning, barrier inhomogeneity and other interface specific effects [32]. Frequency dependence of (*C-V*) characteristics of Pd/ZnO thin film Schottky junction at room temperature is demonstrated in Fig. 5. The graph shows the tendency of decreasing capacitance with increasing frequency, which is evidence for the existence of interface states and its progressive decrease of the response to the applied ac voltage [32]. Carrier concentration, N_d can be determined from the slope of the linear region of reverse bias C^{-2}-V characteristics of diode depicted in the inset of Fig.5. The value of N_d is found to be around 6x10^{14} cm^{-3} at 50KHz, according to the equation (4) [32].

$$\frac{1}{C^2} = \frac{2(V_{bi} + V)}{q\varepsilon_s A^2 N_d} \quad (4)$$

Where, V_{bi} is the built-in potential at zero bias, $_s$ is the dielectric constant of n-ZnO.

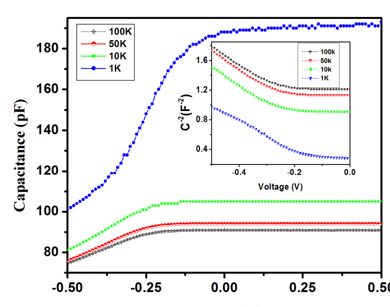

Fig.5. *C-V* Characteristics of Pd/ZnO Schottky diode at different frequencies, the inset shows the corresponding C^{-2}-V characteristics.

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IV. HYDROGEN SENSING CHARACTERISTICS

A. Role of Pd as Catalyst in Sensing

Palladium is one of the most active noble metal catalysts, with high surface energy due to the presence of partially filled valence orbital. It acts as a heterogeneous catalyst that enhances the reaction of adsorbed gas species on solid catalyst surface [33]. Reducing gases like hydrogen and hydrocarbon will get adsorbed on the Pd with the exchange of free electrons (d-band electrons) with the metal surface, leading to its effective dissociation into ions. In this dissociative adsorption process, an exothermic heat of adsorption is involved, which lowers the activation energy and thus accelerating the dissociation [12], [33]. Though the noble metal catalyst like Pd can accelerate the dissociative adsorptions of hydrogen and hydrocarbons very effectively, it cannot accelerate the reaction with oxygen (synthetic air) due to the high activation energy involved in the process [12].

B. Hydrogen Sensing Steady State I-V characteristics

I-V characteristics of Pd/ZnO thin film Schottky diode were measured over hydrogen concentrations ranging from 50 ppm to 1000 ppm in the temperature range of 25°C to 200°C and are depicted in Fig. 6(a-d). It evinced the systematic dependence of diode current on hydrogen concentrations. The lateral shift observed in the I-V characteristics of the diode in the presence of hydrogen is ascribed to the reduction in the barrier height of Pd/ZnO thin film Schottky diode [1], [13]. Hydrogen will undergo catalytic cracking into hydrogen atoms on Pd surface, which will diffuse through Pd, on account of hydrogen concentration gradient and reach Pd/ZnO interface. Further, the hydrogen atoms undergo induced polarization because of the built-in electric field and form dipole layer at the interface. The dipoles thus formed lowers the barrier height and thus accountable for the increase in current upon hydrogen introduction [14]-[19]. The mechanism is illustrated in Fig.7 with the help of energy band diagram of Pd/ZnO Schottky diode.

We have perused the hydrogen sensing *I-V* characteristics of the Schottky diode at different temperatures as given in Fig. 6, following the strategy given in [1] and calculated the key diode parameters such as barrier height, ideality factor, series resistance and saturation current. Fig. 8(a) illustrates that the Schottky barrier height variation, $\Delta\phi_B$ (the difference between Schottky barrier in the presence of air ($\phi_{B,air}$) and Schottky barrier in the presence of hydrogen (ϕ_{B,H_2})) rises rapidly as hydrogen concentration increases and the maximum variation is obtained at 150°C. As hydrogen concentration increases, number of hydrogen atoms, which form dipoles at interface increase leading to an immense reduction in the barrier height [14], [15]. Fig. 8 (b) outlines the influence of hydrogen concentration and temperature on the relative response of the sensor, which is calculated by $R=(\frac{I_{gas}}{I_{air}})$, where I_{gas} is the current in the presence of hydrogen and I_{air} is the current in the presence of air.

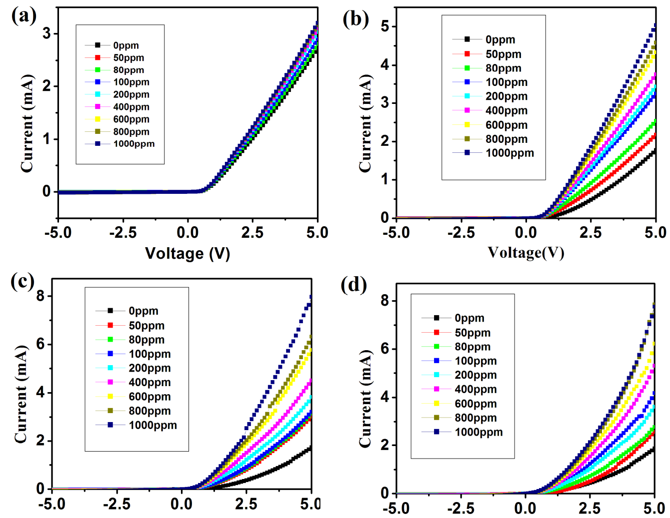

Fig.6. I-V characteristics of Pd/ZnO thin film Schottky diode at different hydrogen concentrations at (a) 25°C, (b) 75°C, (c) 150°C, (d) 200°C.

It is worth noted from Fig. 8 (a) and (b) that the sensor performance enhances, as the temperature increase up to 150°C. This can be briefly explained as follows: as the temperature increases more hydrogen molecules get the energy to overcome the potential barrier for the dissociative reactions on the Pd-ZnO surface. This will, in turn, increases the number of hydrogen atoms reaching the Pd/ZnO interface resulting in a strongly polarized layer at the interface and consequently enhance Schottky barrier height reduction and current. This kind of temperature effect has been observed by Chen et al. [14]. However, the sensor performance has been observed to degrade beyond 150°C and this could possibly be due to the enormous increase in hydrogen atoms over the device surface at high temperatures. This can further cause the absorption of hydrogen into the bulk material leading into the phase transition of Pd metal. The embrittlement effect thus occurred can cause mechanical damage to the layer. Also, it has earlier been reported that hydrogen can induce stress over the palladium surface, which can cause the blistering of the metal. These factors could adversely affect the performance of the sensor over time at high temperature [33].

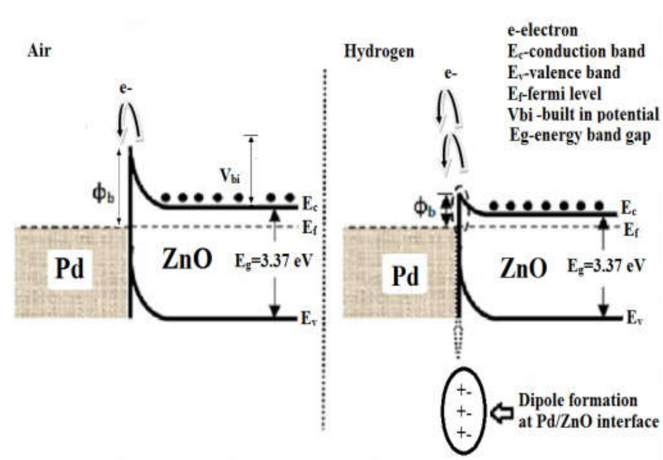

Fig.7. Energy band diagram of Pd/ZnO Schottky diode, illustrating hydrogen sensing mechanism.

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Series resistance is an important parameter which affects the diode characteristic, whose value at different hydrogen concentrations and temperatures are calculated using the slope of *(dv/dlnI) vs. I* curve. Fig. 9 (a) and (b) elucidates the impact of hydrogen concentration on ideality factor and series resistance of the Schottky diode at different temperatures, which was calculated following the standard method described in [1].

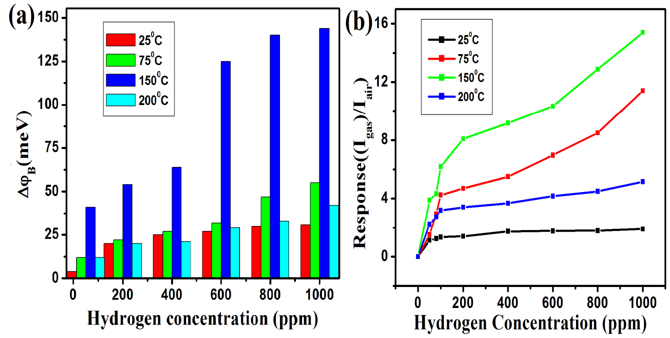

Fig. 8. Hydrogen concentration and temperature dependence of (a) Schottky barrier height variation and (b) Relative response of Pd/ZnO thin film Schottky diode.

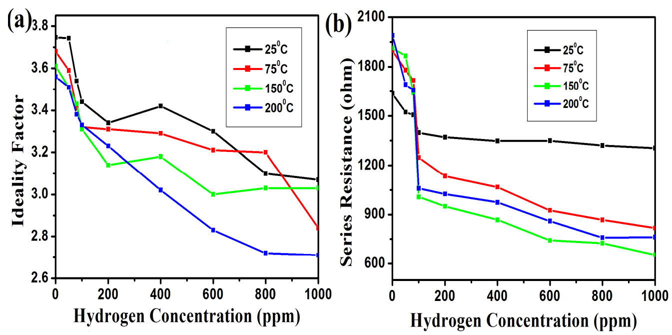

Fig.9. Hydrogen concentration and temperature dependence of (a) Ideality factor and (b) series resistance of Pd/ZnO thin film Schottky diode.

Ideality factor decreases as the hydrogen concentration increase at all operating temperatures. It is interesting to note that diode approaches more ideal thermionic emission behavior as hydrogen concentration increases thus decreasing the value of ideality factor. The reduction of ideality factor of the Schottky diode (in air) as temperature increases, coincide with the observations reported by others for Pd/ZnO Schottky diode [29], [30]. Series resistance of the diode also showed a decrease in its value as hydrogen concentration increase. It is predicted that in the presence of hydrogen, electrons can easily pass through the Pd bulk to the Pd/ZnO interface causing a reduction in the resistance value as hydrogen concentration increases [14].

C. *Hydrogen Sensing Transient Characteristics*

The Fig. 10(a) shows the continuous response-recovery signal of the sample at 150°C when subjected to gas exposure cycles of hydrogen of concentration ranging 50-1000ppm at a constant voltage of 1V. It clearly shows that the response of sample steeply increase with hydrogen concentration. Also, it is observed that the transient response is stable and reproducible in the repeated gas exposure cycles, which can be the outcome of good chemical and thermal stability of sputtered ZnO thin film [7]. The sensor current increases upon exposure to the hydrogen and shows good reversibility in returning to the baseline current upon the removal of hydrogen. The relative sensitivity of the device has been calculated using the equation given below.

$$S(\%) = \frac{I_{gas} - I_{air}}{I_{air}} \times 100 \tag{5}$$

The sample showed very good relative sensitivities in the range of 224% to 1125% upon exposure to hydrogen of concentration in the range of 50 to 1000ppm at 150°C. The excellent hydrogen response we achieved is credited to the high surface to volume ratio of ZnO thin film, along with the catalytic activity of palladium dots. The response time is defined as the time taken to reach 90% of saturation current after the target gas was introduced and the recovery time is defined as the time taken to return to 10% of baseline current after the target was removed. We have obtained a considerably good reaction kinetics speed with response time ranging from 55 to 115 seconds and recovery time ranging from 58 to 26 seconds as hydrogen concentration increases from 50 to 1000 ppm. It is reported that the response time of gas sensors is proportional to particle size of sensing element and hence shorter response time is expected for the sensor that uses nano-sized particles as sensing element [28]. The shorter response and recovery time at high temperature (150°C) can also be due to the defects and interface states at Pd/ZnO surface as they make the surface unstable and reactive to oxygen and reducing gasses, leading to fast adsorption and desorption process [34]. To check the reproducibility and stability of the proposed device, we have considered four cycles of measurement of about 55 minutes duration at 100 ppm hydrogen, which is shown in Fig. 10 (b). We have repeated the response-recovery measurements, after a gap of one month from the initial testing (inset of Fig.10 (a)) and have obtained better consistency without much degradation. The proposed sensor is highly stable and suitable for commercial purposes as the results are reproducible after several cycles and after a period of one month.

D. *Surface Reactions Involved*

Apart from the barrier height lowering at the Pd/ZnO interface, surface controlled reactions upon adsorption and desorption of target gas on ZnO thin film surface also contributes to the hydrogen sensing characteristics. This phenomenon is ascribed in the literature to the following surface chemistry model: when the Pd/ZnO surface is exposed to synthetic air, oxygen will get adsorbed on the ZnO surface and electron transfer will occur from conduction band of ZnO to adsorbed oxygen atoms following the generation of ionic species like O_2^-, O^- and O^{2-}. This creates a space charge region and the potential barrier associated with it lowers the electrical conductivity of ZnO thin film surface. The Pd dots on ZnO surface can enhance the oxygen spill over process, by providing a lower energy pathway for the gaseous species.

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It will increase the number of chemisorbed oxygen atoms on ZnO surface. Also, sufficient area of ZnO thin film surface is uncovered in the device structure to facilitate direct oxygen chemisorptions [34], [35]. The corresponding reactions involved are depicted as

$O_{2gas} + e^- \rightarrow O^-_{2(ads)}$, $O^-_{2(ads)} + e^- \rightarrow 2O^-_{(ads)}$, $2O^-_{(ads)} + e^- \rightarrow O^{2-}_{(ads)}$

On the other hand, increase in the electrical conductivity or sensor current upon exposure of sensor to reducing gases like hydrogen can be explained as follows: Pd metal dots on ZnO thin film surface facilitates the catalytic decomposition of hydrogen molecules into hydrogen atoms and can further activate its spill over process on ZnO surface [9], [24]. The hydrogen atoms then undergo surface reactions with chemisorbed oxygen ions causing the subsequent donation of trapped electrons to the conduction band of ZnO, which is well explained by the forthcoming equations [9],

$4H + O_2^- \rightarrow 2H_2O + e^-$, $2H + O^- \rightarrow H_2O + e^-$, $2H + O^{2-} \rightarrow H_2O + 2e^-$

More precisely, the modulation of space charge region on ZnO thin film surface due to gas interactions also reflects in the transient sensing characteristics of the sensor.

The empirical relation for the sensitivity, S_g as a function of hydrogen concentration can be given as in (6)

$$S_{(g)} = A(P_{(g)})^{\beta} + 1 \qquad (6)$$

Where, A and β are empirically obtained parameters, that depends on the stoichiometry of surface reactions and charge of surface species involved in gas sensing, $P_{(g)}$ is the target gas concentration that is proportional to the gas concentration. It was reported that β is 0.5, if the adsorbed oxygen species is O^{2-} and is 1 if the dominant adsorbed species is O^- [34]. The equation (6) can now be expressed as following.

$$\log(S_g - 1) = \log A + \beta \log C_{(g)} \qquad (7)$$

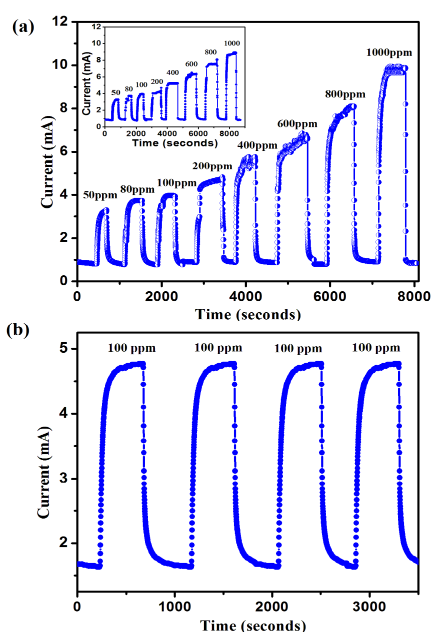

Fig.10. (a) Continuous response- recovery characteristics of sensor at different hydrogen concentrations at 150°C, inset provides the response curve after a gap of one month.(b) Dynamic characteristics showing repeatability of sensor at hydrogen concentration of 100 ppm.

Fig. 11 depicts the plot of *log* $(S_g$*-1) vs. log* C_g, from which the slope is obtained as 0.53, which suggests that the dominant adsorbed oxygen species on the ZnO thin film surface is O^{2-}. The presence of a large amount of highly reactive oxygen ion (O^{2-}) compared to less reactive single negative oxygen ions could also be a possible reason for the excellent sensitivity of the proposed sensor [32].

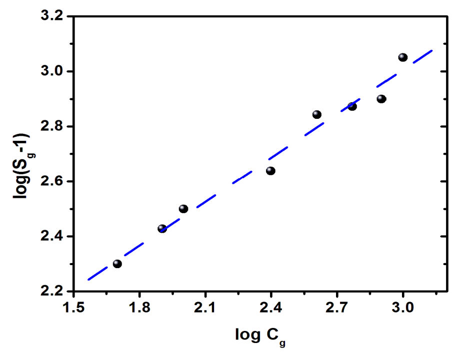

Fig.11. Log (S_g-1) vs log C_g plot for hydrogen sensing.

To gain insight towards the selectivity of the proposed sensor towards other gasses, we have considered one hydrogen-containing gas, methane and an oxidizing gas, nitrogen dioxide. The results obtained shown in the Fig.12, illustrates that the sensitivity of device towards methane is ten times lesser compared to hydrogen sensitivity. Table. I provide the sensitivity values obtained when the sensor is exposed to hydrogen and methane. The inset of Fig.12 depicts the response of device towards nitrogen dioxide, which confirms that the device is insensitive to oxidizing gases like nitrogen dioxide.

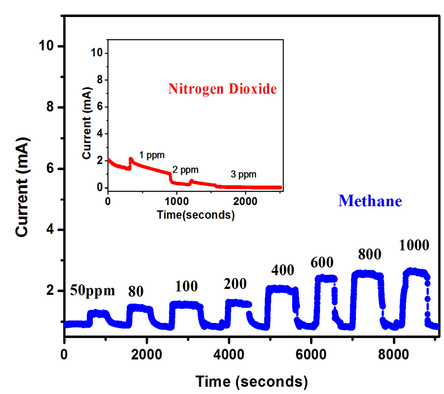

Fig.12. Continuous response- recovery characteristics of the sensor at different methane concentrations, inset, provides the response of sensor towards nitrogen dioxide.

TABLE. I
HYDROGEN AND METHANE SENSITIVITY

Concentration (ppm)	50	80	100	200	400	600	800	1000
Hydrogen Sensitivity (%)	224	268	317	437	697	745	795	1125
Methane Sensitivity (%)	41	61	72	76	98	115	121	132

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TABLE. II
PERFORMANCE COMPARISON ON PREVIOUSLY REPORTED ZnO BASED HYDROGEN SENSORS

Device structure	Concentration of H_2 and temperature	Sensitivity	Response/Recovery time	Method of ZnO deposition	Reference
Pt/ZnO thin film/SiO_2/Si	200ppm/350°C	98%	-	RF Sputtering	[20]
ZnO nanowire array	100ppm/250°C	98%	60sec/14sec	Hydrothermal technique	[36]
Pd-Ag/ZnO /PS/Si/Al	1%/150°C	61%	93/445sec	Sol-gel dip coating	[37]
Pd coated ZnO nanorod	500ppm/RT	4.2%	-/few minutes	Molecular beam epitaxy	[38]
Pd/ZnO thin film Schottky diode	50ppm/150°C	224%	55/58sec	RF Sputtering	Our work
	1000ppm/150°C	1125%	115/26 sec		

Table. II show the performance comparison of previously reported ZnO based hydrogen sensors. It is evident from the table that, performance of our proposed sensor is superior to many of the previous works [20], [36]-[38]. We have obtained excellent sensitivity and fast response/recovery. Also our device is proven to have good selectivity to hydrogen over hydrocarbons like methane and oxidizing gasses like nitrogen dioxide. It is also having the advantage of simple and easy to fabricate structure, without any additional electrical contacts, and hence it possesses great prospect for practical hydrogen sensing applications.

V. CONCLUSIONS

A detailed investigation has been performed on the hydrogen sensing properties of the proposed sensor formed by incorporating several palladium Schottky contacts on RF sputtered ZnO thin film on Si substrate. Lateral shifts have been observed in the steady-state *I-V* characteristics of the sensor at different temperatures and hydrogen concentrations. The optimum performance of the sensor has been obtained at 150°C with maximum SBH variation of 144 meV at 1000 ppm hydrogen. The maximum sensitivity of 1125 % has been obtained at 1000 ppm hydrogen. A detailed discussion of the main principles underlying the observed gas sensing behavior of the device, involving the Schottky barrier height variations and Pd-catalyzed electrical conductivity variations of the ZnO thin film surface have been presented. Electrical characterizations of Pd/ZnO thin film Schottky junctions have also performed to confirm the formation of good Schottky contact. Moreover, the basic microstructure study of ZnO thin film has also been undertaken. Results obtained so far, reveal the huge prospective of Pd/nanocrystalline ZnO thin film Schottky diode for developing economical, simple and highly efficient hydrogen sensors.

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