# The Effect of Catalytic Metal Contact on Methane Sensing Performance of Nanoporous ZnO -Si Heterojunction

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***Abstract- A sol-gel derived ZnO-p-Si heterojunction structure were fabricated and investigated as a potential methane sensor. Three configurations with different contacts (Pd-Ag contact both on ZnO and Si / Pd-Ag on ZnO side and Au on Si / and Au on both sides of the junction) were fabricated in order to study the impact of the catalytic contact on the methane sensing properties. Structural characterization with high resolution FESEM and EDX study revealed the synthesis of highly crystalline ZnO thin film with particle size ~40nm. The catalytic contact metal used was also of nanoporous nature as was revealed from FESEM were as the noncatalyic metal showed flake like texture. The heterojunctions were investigated at different operating temperatures (50$^{o}$C-300$^{o}$C) and at different operating voltages (1-5V) for varying concentrations of methane (0.1%, 0.5% and 1.0%). It was observed that the device with Pd-Ag (70%) contacts on both sides offered shorter response time (~28sec) and much higher response magnitude (~63%) compared to the sensor with Au contact both sides (response time ~47 sec and response magnitude ~ 19%). It is further revealed that the sensor performance with catalytic contact only to ZnO (and Au to Si) is almost the same as that of sensor having catalytic contact on both sides, emphasizing the fact that using catalytic contact to the sensing layer only modulates the sensor characteristics. The diode parameters like ideality factor, saturation current and the change in barrier height (upon exposure to methane) were also calculated for getting the insight of the sensing mechanism and were found to be in well agreement with the experimental results.***

**Keywords- Sol-gel, ZnO, Heterojunction devices, Methane sensor, Pd-Ag (70%) catalytic contact**

## I. INTRODUCTION

ZnO thin films have been an active field of research because of its applications in sensors/ transducers [1], optoelectronic devices [2] and SAW devices [3]. ZnO is an n-type II-VI compound semiconductor having a wide band gap (~3.3eV), which makes good heterojunction [4] with p-type silicon (Eg~1.1Ev). These heterostructures are very effective in gas sensing applications [5]. Many works have already been reported on the fabrication of ZnO thin film via several routes such as sputtering [6], spray pyrolysis [7], CVD [8], sol–gel [9] and galvanic deposition technique [10] etc. Among all the techniques sol gel gives good control over the morphology, particle size and thickness of the ZnO. As there exists fairly good (3.31%) lattice matching between ZnO and Si ZnO makes a good heterojunction with p-Si [5]. Moreover sol gel grown ZnO has already been reported to show good performance in gas sensing applications [11]. Another advantage with the sol-gel process is its CMOS compatibility [12].

For detection of various harmful or explosive gases resistive semiconductor gas sensors have been advancing in the last few years [13-15]. Among the various target gases methane sensing is of special interest due to its importance in coal mines, greenhouse emission and as major component of LNG/CNG [11, 12]. Metal oxides like $SnO_2$, $WO_3$, $Ga_2O_3$ , $TiO_2$ , ZnO etc. as the sensing material [16-21] has been well investigated. The benefits of these sensors are, mainly, the cost-effective fabrication, combined with possibilities for system-on-chip solutions for processing of the measurements. Most of these methane sensors were operated in the resistive mode [21, 22]. Though there are report on metal-Insulator-metal (MIM) sensor structure also [22, 23].P. Bhattacharyya et. al [4] investigated ZnO-Si based methane sensor which was based on galvanically deposited ZnO thin film and suffers from the problem of longer response time probably due to the non-porous compact structure of the sensing film. In this report we present ZnO-Si heterojunction sensors for methane detection based on sol-gel grown nanoporous ZnO sensing layer.

In this paper we report a sol gel grown nanocrystalline nanoporous ZnO-p-Si heterojunction based methane sensor and study the effect of contact metals [Pd-Ag (70%) and Au] on the sensor performance. The impact of Pd-Ag catalytic contact has been reported to improve the sensing

performance of such sol-gel grown ZnO-p-Si heterojunction sensors through the mechanism of barrier modulation [24, 25]. In earlier reports Pd-Ag (26%) alloy were used to fabricate the catalytic contacts [4, 12, 21-23] but in this report we investigated a different composition Pd-Ag (70%) alloy to envisage its impact on the sensor characteristics. In order to understand the impact of the (Pd-Ag)-ZnO junction in particular we have explored the impact of variation of contact material on the ZnO side of our device as well as the Si side. The I-V characteristic of the sensor has been studied at different operating temperatures (50,100,150,200,250,275 and 300$^{o}$C) with and without the presence of 1% methane. The optimum voltage and temperature for all 3 types of device configurations as well as their response and recovery time at optimized parameters (temperature and voltage) were calculated. It was observed that the device with Pd-Ag contacts on both sides offered shorter response time (~28sec) and much higher response magnitude (~63%) compared to the sensor with Au contact both sides (response time ~47 sec and resp magnitude ~ 19%) but it didn't differ much in terms of performance from that of Pd-Ag on ZnO side and Au contact on the Si. This emphasizes the importance of the (Pd-Ag) catalytic contact as well as utility of using such contacts to sensing layer only. The diode parameters and the barrier height were also calculated for all the three ZnO based Schottky devices to justify the experimental results.

## II. EXPERIMENTAL

Nanocrystalline ZnO thin films deposited on p-Si<100> substrates by sol-gel method similar to that reported earlier by Bhattacharyya et. al [11,12, 21] Zinc acetate dihydrate [$Zn(CH_3COO)_2$-$2H_2O$] and Diethanolamine (DEA) precursors in an isopropyl alcohol (IPA) medium was used to form the sol. 0.6gm Zinc Acetate was thoroughly mixed in 50cc isopropanol by stirring at room temp (24$^{o}$C) for 1Hr. Drop-wise diethanolamine (DEA) was added to this milky white solution to yield a clear transparent homogeneous solution and the resulting mixture was further stirred for 1 Hr. After aging for 24 h, the solution was subjected to spin coating on p-Si <100> (resistivity 1 Ω cm, 400 μm thick) substrates with a dimension 5 mm × 5 mm. The rotation speed of the coating unit was 1000 r.p.m and the duration of the spin was 30 s. Then the samples were baked at 110$^{o}$C for 10 min to evaporate the solvent and to remove organic residuals. Finally the samples were annealed at 600$^{o}$C in air for 1 hr for to produce nanocrystalline ZnO. The entire

process (spin-coating & annealing) was repeated for three times to produce a ZnO film of ~900 nm thickness [11, 12].

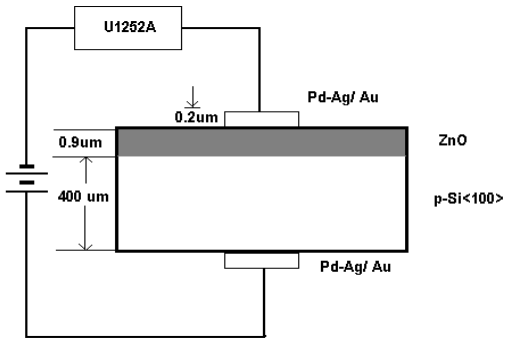
The detailed structural analysis e.g. Energy Dispersive X-ray (EDX) and Field emission Scanning Electron Microscopic (FE-SEM) of the nanocrystalline ZnO films produced by sol-gel method was performed to study the crystal size, surface morphology and pore size of the deposited ZnO thin films. FESEM images also demonstrate the nanocrystalline and nanoporous characters of the various metal contacts used as electrode on ZnO surface.

The Pd–Ag (70%) catalytic metal contacts and Au metal contacts (both of 2mmx2mm dimension) of thickness ~0.2micron was deposited on the sol-gel ZnO thin films and on the Si substrate by e-beam evaporation ($10^{-6}$ mbar) using an Al metal mask. Three classes of samples were prepared by taking three different combinations of the contacts e.g. 1) S1- sample with Pd-Ag contacts at both the sides, 2) S2-sample with Pd-Ag contact at ZnO and Au at silicon and 3) S3- sample with Au contacts at both the sides. The electrical contacts were taken from contact pad by using fine copper wire and silver paste. The schematic of the gas sensor structure with requisite dimensions is shown in Fig.1 (a)

The sensor characteristics were studied inside a closed corning glass tube (10 cm × 4 cm) with inlet and outlet for gases and it was placed horizontally and coaxially inside a resistively heated furnace with a 4 cm constant temperature zone. The temperature was controlled within ±1°C using a copper constantan thermocouple in-built in a precise temperature controller. For sensor study high purity (100%) methane gas and IOLAR grade $N_2$ in desired proportions were allowed to flow to the gas-sensing chamber through a mixing path via Alicat Scientific mass flow controller & the mass flow meter, respectively. The mass flow rate and thus the relative concentrations of the gases were kept constant throughout the experiment. The gas pressure over the sensor device was 1 atmosphere during the experiment. I-V characteristics of each sample at the different operating temperatures (50,100,150,200,250,275 and 300$^{o}$C) in pure $N_2$ and in 1% methane in $N_2$ were studied. The transient response characteristics for concentrations of 0.1%, 0.5% and 1.0% methane at different operating temperatures were also studied. The current was measured by an Agilent U1252A multimeter.

## III. RESULTS AND DISCUSSIONS

### STRUCTURL CHARACTERIZATION

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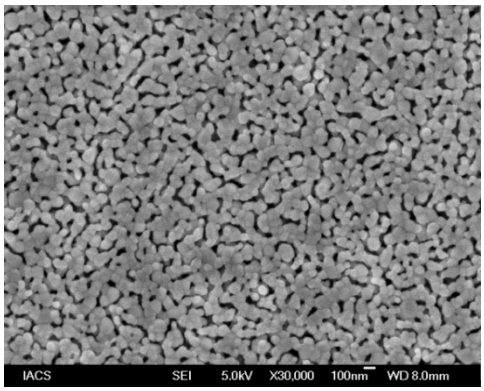


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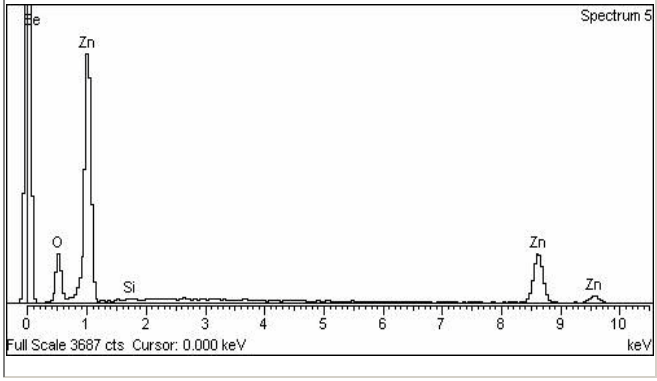
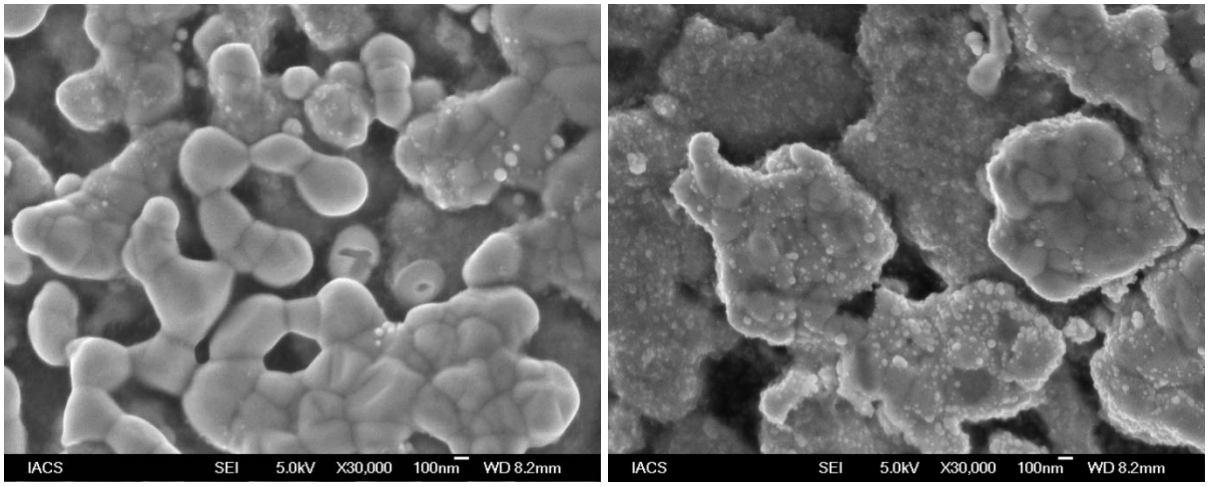



| Element | Weight% | Atomic% |
|---|---|---|
| O K | 24.81 | 57.25 |
| Si K | 0.37 | 0.49 |
| Zn K | 74.82 | 42.26 |
| Totals | 100.00 | |

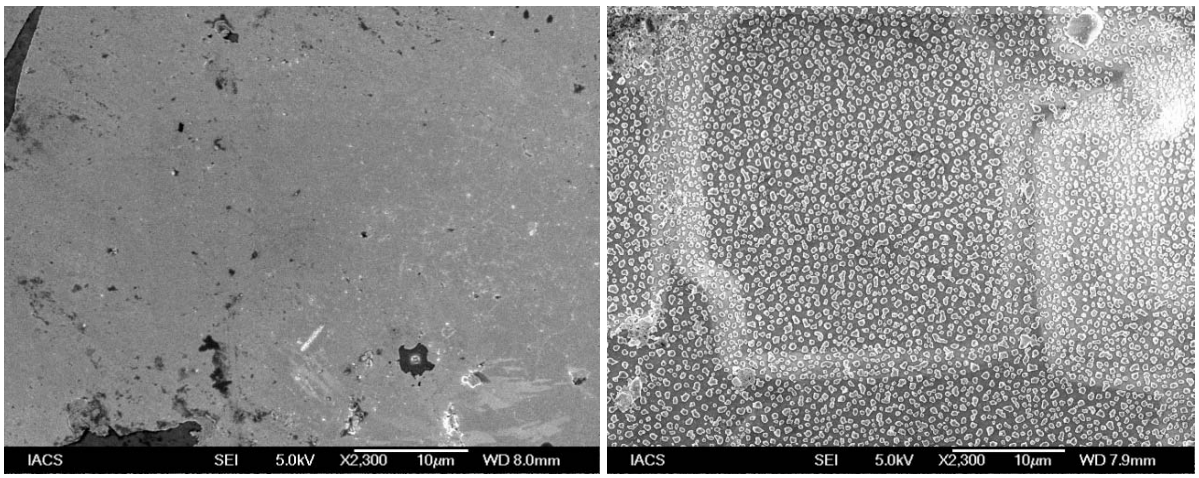
(c)

Figure 1**.** (a) Schematic of the heterojunction device (b) FESEM image of sol-gel derived ZnO and (c) EDX results of the ZnO thin film.

Fig 1(b) & 1(c) shows the FESEM and EDX images of ZnO on Si surface. From the FESEM (Jeol JSM-6700F, used 5 kV and 10μA) images and EDX (Oxford Instruments, INCA) studies it was evident that highly crystalline ZnO was formed on the p-Si<100> substrates by sol-gel technique as described earlier [11]. FESEM images suggest the particle size of the ZnO to be ~40-50 nm whereas EDX indicate the overall presence of (by weight) 74.82% Zn and 24.81% O in the sample under study. FESEM of the metallic contact pads was also done in order to get the insight into nano-structure of catalytic contact. Electrical contacts on the ZnO side of the sample show a very porous flaky nature for both Au and Pd-Ag(70%) metal while the contacts on the Si side are less porous (shown in Fig 2 (a) – 2(d)). This porous nature also goes to take a very significant role regarding the chemisorptions kinetics of methane.



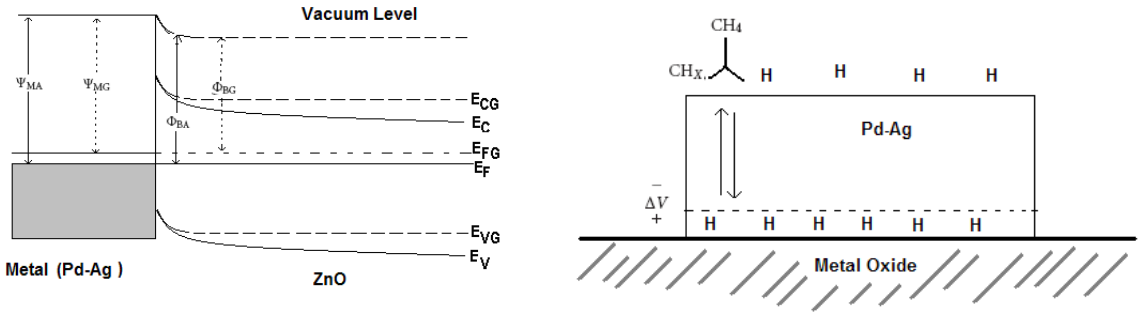

(a) (b)




(c) (d)

Figure 2**.** FESEM images of the (a) Au contact on ZnO (b) Pd-Ag (70%) on ZnO (c) Au on Si and (d) Pd-Ag(70%) on Si

The use of Pd-Ag(26%) catalytic contact metal on nanocrystalline ZnO thin films to improve methane detection properties of such sensors has been reported [4, 22-25] earlier. Pd acts as a very good catalyst by forming weak bonds with ambient oxygen at elevated temperatures. For methane sensing with such catalytic contacts the dissociative adsorption of methane at the catalytic metal surface is followed by reaction of $CH_3$ or H with the atomic oxygen adsorbed on the Pd metal surface to produce water. It is this production of water that leads to blistering of Pd thin films for repeated sensing cycles. In order to stop the blistering (and subsequent chip-off) and also retard the phase transition due to the formation of Pd-H, Pd-Ag alloy is preferred as contact material in sensor applications. [24, 25].




(a) (b)

Figure 3**.** (a) Schematic band diagram of a typical metal semiconductor Schottky barrier showing band bending upon exposure to methane $\psi_{MA}$, $\psi_{MG}$ are the work function of M in air (in pure N2 in our case) and in gas respectively. $\Phi_{BA}$, $\Phi_{BG}$ are the barrier height of the junction in air (in pure N2 in our case) and in gas, respectively. $E_C$, $E_{CG}$ is the conduction band in air (in pure N2 in our case) and in gas, respectively. EV, EVG are the valence band in air (in pure $N_2$ in our case) and in gas, respectively. $E_F$, $E_{FG}$ are the Fermi level in air (in pure N2 in our case) and in gas, respectively. (b) Schematic showing the diffusion of hydrogen through the noble metal and formation of dipole layer across the noble metal/ metal oxide junction.

Another important aspect of catalytic metal contact is the ability of Hydrogen to diffuse through the metal-ZnO interface and reduce barrier height through the formation of interfacial dipole layer. This hydrogen (diffused) also passivates the metal-metal oxide interface and prevents the pinning of the Fermi level thereby aiding in barrier modulation. The silver in Pd-Ag alloy is understood to hinder the diffusion of hydrogen through the noble metal cluster [25]. Hence it is expected that the Pd-Ag (70%) alloy may have slightly higher operating temperature and take slightly longer to respond compared to the earlier reported [11] Pd-Ag (26%) alloy.

Also an important factor is the porosity of the Pd-Ag catalytic contacts. In compact contact films gases cannot penetrate deep into the catalytic metal and the gas sensing reaction reduced, but through the nanoporous metal layer (as revealed from fig. 2(b) the catalytic metal layer is porous in this case), gas molecules can access almost the entire volume of the catalytic metal thin film and the gas sensing reaction can, therefore, take place with much ease. Also the trapping of gas molecules in these nanopores can be very helpful in increasing the response magnitude.

## STUDY OF I-V CHARECTERISTICS

To get the optimum operating voltage and temperature in terms of response magnitude the I-V characteristics of the sensor with different contacts were studied in pure N2 and in 1% methane. The current was recorded at different temperatures ($50^oC$ to $300^oC$). Figure (4) shows the forward bias I-V characteristics of the junction with Pd-Ag(70%) and Au contacts in pure N2 at different temperature. The rectifying

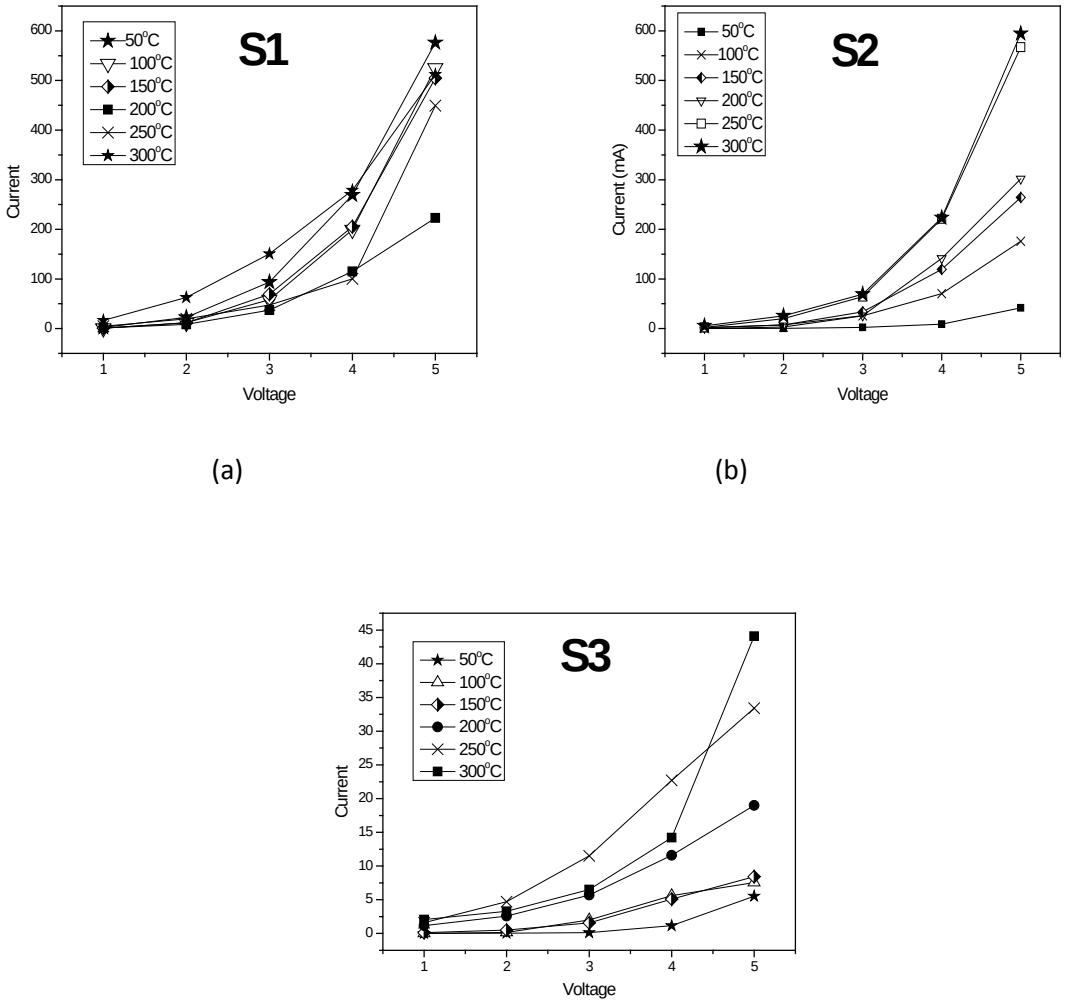



Figure 4**.** I-V characteristics of ZnO/Si heterojunction in pure N2 at different temperatures for (a) Pd-Ag(70%) contact both sides (S1) (b) Pd-Ag(70%) on ZnO and Au on Si (S2) and (c) Au contacts both side (S3)

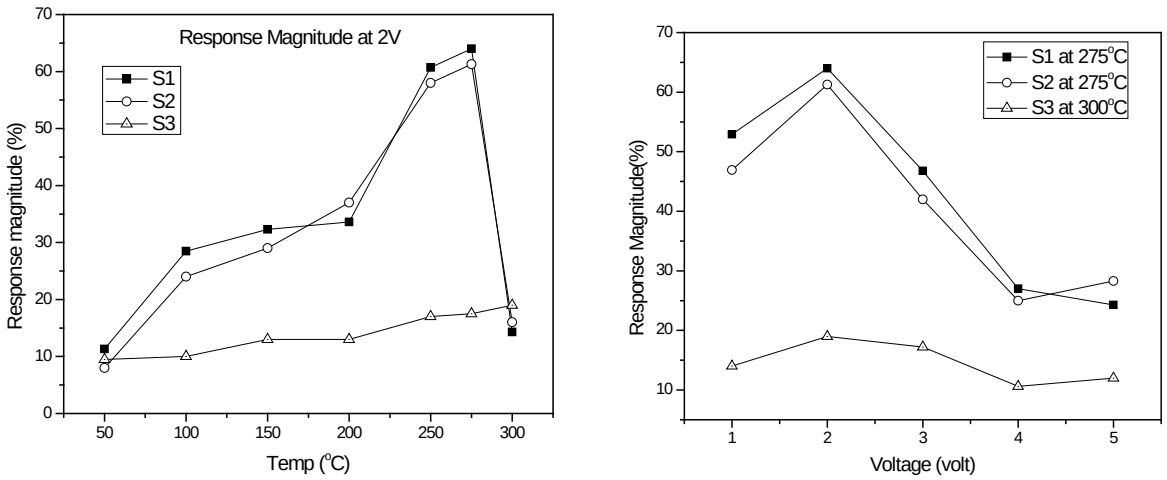
character of the junctions (specially in case of higher operating temperature) is clearly seen from all three graphs. It is worth noting that the currents for the samples S1 and S2 are many times higher compared to that for S3. The possible reason behind this is probably owing to the higher Schottky barrier height (SBH) for Au-ZnO contact ( higher by an amount of 0.1-0.2eV) compared to that of Pd-ZnO (or in this case Pd-Ag-ZnO) Schottky barrier as already reported by

P. Klason [26] and W.Mtangi [27]. There was almost no change in the reverse current upon exposure to gas that is why only forward current has been plotted here.

The response magnitude in terms of the forward bias current of the sensor is calculated as [4]

$$RM = \frac{I_g - I_a}{I_a}$$

Where $I_g$ is the current in the test gas and $I_a$ is the current in air (in pure $N_2$ in our case).



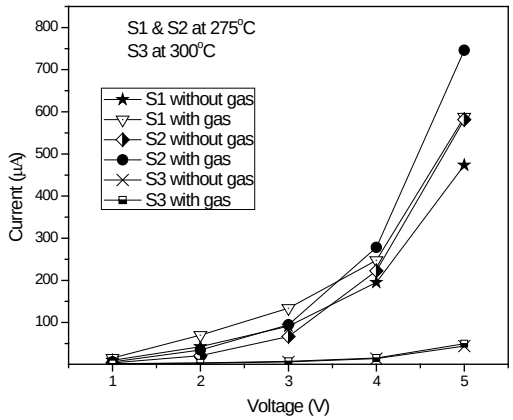

(a) (b)

Figure 5**.** Variation of response magnitude with (a) operating temperature and (b) applied voltage

As per the above equation the response magnitude of the heterojunction with different contacts were calculated at different temperature. Figure (5) shows the response magnitude at optimum voltage and temperature. This clearly shows that for all the three types of devices the maximum response magnitude was exhibited at approximately 2V, (which is in well agreement with the earlier reports [4] regarding such heterojunction devices) and the sensing temperature of the junction also varies with the contact. i.e the optimum temperature for the S1 and S2 were found as 275$^o$C in contrast to 300$^o$C for S3. Due to the catalytic effect of Pd-Ag (70%) contact the optimum operating temperature of S1 and S2 was lower compared to S3 with Au contact. Also notable is that this operating temperature of 275$^o$C is higher than that one of 250$^o$C reported earlier for Pd-Ag (26%) contacts [4]. The Pd-Ag contact at the ZnO sensing layer gives the

maximum sensitivity (approximately 63%) where as the response magnitude with Au contact on ZnO reduces drastically (19%). It was observed that the device with Pd-Ag(70%) contacts on both sides offered much higher response magnitude (RM) (~63) compared to the sensor with Au contact both sides (response magnitude ~ 19%) but it didn't differ much in terms of performance from that of Pd-Ag on ZnO side and Au contact on the Si (Response magnitude ~61%).

## STUDY OF TRANSIENT CHARECTERISTICS

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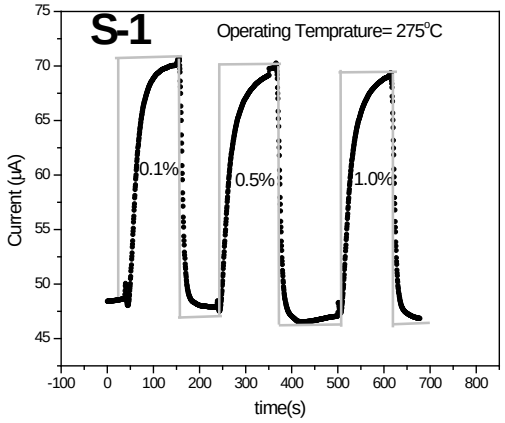


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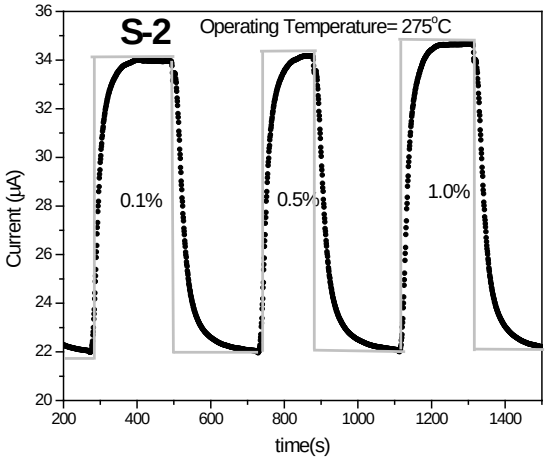


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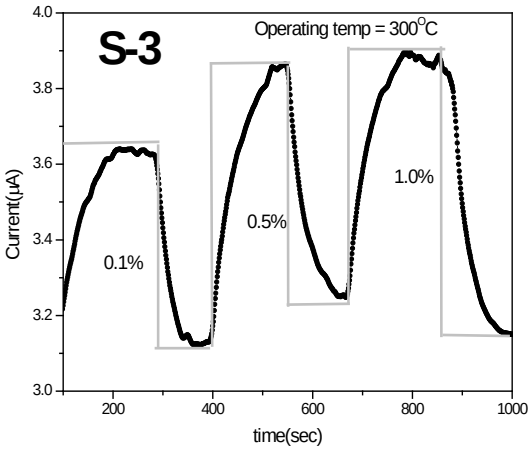


(d)

Figure 6**.** (a) I-V characteristics in pure N2 and in 1% methane concentration for optimized operating temperature and voltages for the different devices; and Transient response characteristics for (b) both side Pd-Ag(70%) (c) ZnO side Pd-Ag and Si side Au & (d) both side Au.

The transient response characteristics of the heterojunction were studied at the operating temperatures with three different concentrations of the methane (0.1%, 0.5%, 1.0%). Figure (6) shows the same for three different combinations of the contacts. From the nature of the curve it is understood that the current first increases and then saturates when the sensor exposes towards methane and cutting off the methane supply as results decrease of the current towards the base line. In some part of the figure it is not coming exactly to the base line which may be attributed to the of the hysteresis effect. Experimentally it is found that for all the three types of samples reduction of the gas concentration bellow 1% results no significant change in the flow of current level and increase of the concentration above 1% gives the response which is quite alike of the result at 1%, implying saturation of adsorption sites above 1.0% concentration level.

The response time of the sensors were measured as time taken to reach 67% of the saturation value (value after exposure to methane) and the recovery time was defined as 67% of the time taken to reach back to the original value (value before exposure to methane). From the transient response, it was calculated that the device with Pd-Ag (70%) contacts on both sides offered shorter response time (RST~28sec at operating temperature of 275$^{o}$C) compared to the sensor with Au contact both sides (response time ~47 sec at operating temperature of 300$^{o}$C) but it didn't differ much in terms of performance from that of Pd-Ag (70%) on ZnO side and Au contact on the Si. (Response time ~30 at operating temperature of 275$^{o}$C). This emphasizes the importance of using Pd-Ag (70%) contact to ZnO side only for improvement of gas sensing performance.

Table (1) and figure (7) shows the values and bar diagram of the response magnitude (RM), response time(RST) and recovery time(RCT) of the sensor at their respective operating temperature for three different methane concentrations

Table 1**.** Measured sensor study results for the optimized operating temperatures

| **S1** | | | | | **S2** | | | | | **S3** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Op. Temp | Conc. (%) | RM (%) | RST (sec) | RCT (sec) | Op. Temp | Conc. (%) | RM (%) | RST (sec) | RCT (sec) | Op. Temp | Conc. (%) | RM (%) | RST (sec) | RCT (sec) |
| 275°C | 0.1 | 45.8 | 42 | 48 | 275°C | 0.1 | 44.5 | 41 | 50 | 300°C | 0.1 | 7.0 | 53 | 67 |
| | 0.5 | 52.2 | 35 | 39 | | 0.5 | 50.0 | 36 | 41 | | 0.5 | 10.0 | 49 | 71 |
| | 1.0 | 63.9 | 28 | 30 | | 1.0 | 61.2 | 30 | 37 | | 1.0 | 19.0 | 47 | 75 |

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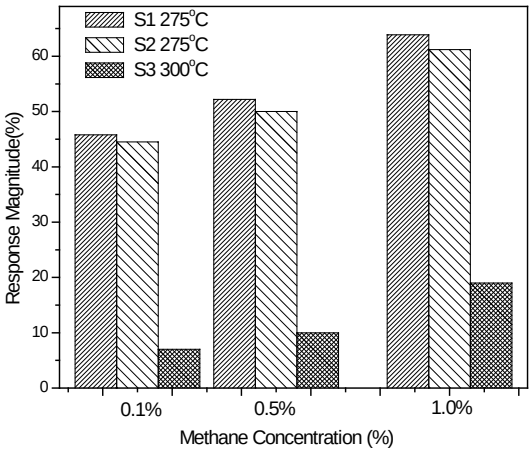
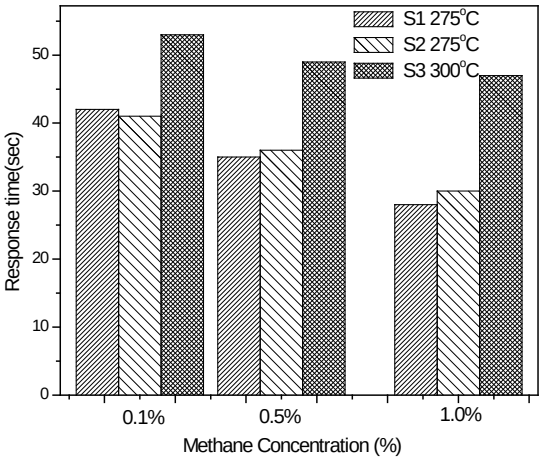



(a)

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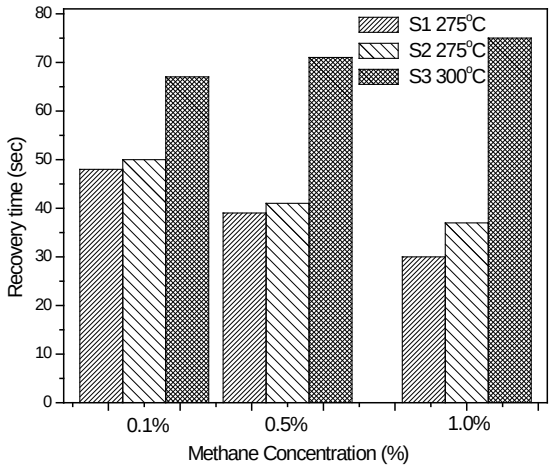



(c)

Figure 7**.** Comparison charts for (a) Response magnitude (b) Response time and (c) Recovery time for the three sensors at optimized parameters

It is evident that with increase in the gas concentration the response time of the sensor reduces where as the recovery time increases. Increase in the concentration of the methane results in adsorption of more methane molecules by the oxide surface leading to the increase in sensor response with decrease in the response time (due to faster electron transport kinetics at higher concentrations [11]). The decrease of the recovery time results due to requirement of additional thermal energy by the sensor for the adsorption of gas molecules by the sensor surface. Out of all the three types of contact the Pd-Ag(70%) shows significant results in terms of response time and recovery time (i.e 28 sec and 30 sec respectively).

In earlier report [4] of galvanic ZnO-p-Si heterojunction using Pd-Ag(26%) contacts the response time was ~100 sec with response magnitude ~46% when exposed to 1% methane at the operating temperature of 250$^{o}$C. In our experiment we have found that the sol-gel grown ZnO-p-Si device offers much faster response (~28 sec) with higher response magnitude (~63%) for the same concentration (1%) of methane but at a slightly higher operating temperature of 275$^{o}$C. This may be attributed to the fact that the higher degree of porosity and the non-stoichiometry of the sol gel deposited ZnO makes it more suited for gas sensing applications compared to galvanic ZnO. Moreover Pd-Ag (26%) catalytic contact is more efficient than Pd-Ag (70%) contact in reducing the operating temperature of sensing due to higher concentration of Pd.

## CALCULATIONS OF SATURATION CURRENT AND BARRIER HEIGHT

From the I-V characteristics of the heterojunction the saturation current and barrier height can be calculated using the relationship

$$I = I_o exp\left(\frac{qV}{\eta kT}\right)$$

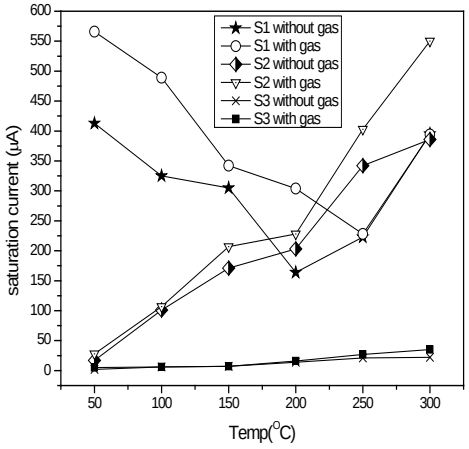
Where $\eta$ is the ideality factor of the diode, T is temperature in Kelvin, k is Boltzmann constant and $I_o$ is the saturation current.

For a diode the saturation current Io represented as

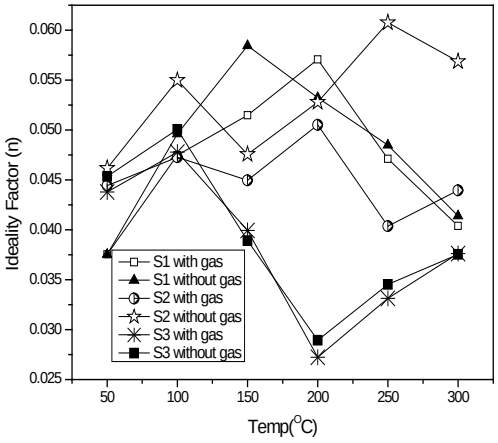
$$I_0 = AA^* T^2 \exp\left(^{-q\phi}/_{kT}\right)$$

Where A is the contact area, A* is the effective Richardson constant and $\phi$ is barrier height.

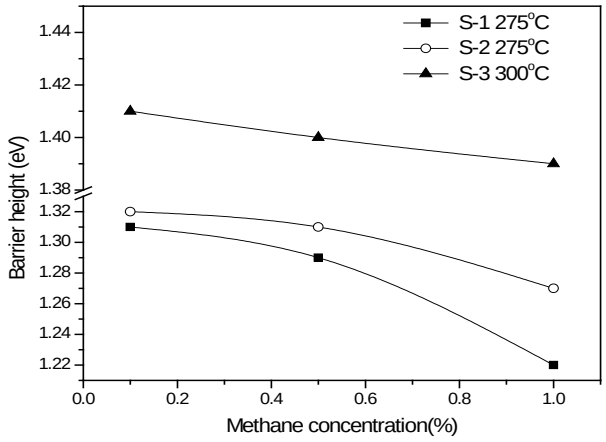
The variation of the saturation current and ideality factor with operating temperature and variation of barrier height with the methane concentration are shown in Figure (8)




(a)




(b)




(c)

Figure 8**.** Variations of (a) saturation current (b) calculated ideality factor with temperatures and (c) variation of barrier height with methane concentration for all three sensor.

It is seen that the ideality factor of all the devices (with and without gas) lies within the range of 0.025-0.06. S1 and S2 showed higher ideality factors (>0.045) compared to S3 for temperatures above 150$^{o}$C. Such overall values indicate the formation of good quality heterojunction. The sudden variations in the nature of the ideality-temperature plot (as evident in Fig 8 (b) can be attributed to the instabilities provided by the interfacial dipole layer created due to the H diffusion through the Pd-Ag, which makes the behavior of the curves for S1 and S2 quite different from S3 in which no Pd-Ag contact is involved [24, 27]. These factors also influence the variation in saturation current. The saturation current seems to be steadily increasing with increase in temperature for S2 and increases slightly for S3. However for S1 the saturation current decreases initially and then suddenly increases above 200$^{o}$C. This behavior is rather different from S2 and S3 (which have Au contact on Si side) and may be due to the presence of Pd-Ag contacts on Si side. The values of the ideality factor and saturation current for the devices involving Pd-Ag (70%) (S1 & S2) seems to be high compared to one for the Au contact on both sides. All the three samples showed band bending with increasing methane concentration. The change in barrier height for Pd-Ag contact samples were much higher than that of Au samples thus explaining the difference in response magnitude. The barrier height is found to be the lowest at 1% methane concentration (for all three samples) this is consistent with the response

magnitude of all the three types of samples found maximum at that concentration. Barrier height of S3 is found to be about 1.39 eV compared to 1.23 eV for S1 and 1.27 eV for S2 at 1.0% methane at their corresponding optimum operating temperature. This emphasizes the fact that (Pd-Ag)-ZnO junction have lesser Schottky barrier height (SBH) at 275$^{o}$C compared to those of Au-ZnO junction at 300$^{o}$C, thus providing an explanation for the much higher values of current found in the I-V characteristic of the devices. The change in barrier height is larger in case of S1 and S2 compared to that of S3 justifying the experimental results of higher response magnitude of S1 and S2 compared to S3.

## IV. CONCLUSION

A ZnO-p-Si<100> heterojunction based sensor for the detection of methane was fabricated and tested for three different methane concentrations (0.1%, 0.5% and 1.0%) at different operating temperatures (50°C-300°C) and operating voltages(1-5V). Three device configurations (Pd-Ag contact on both sides/ Pd-Ag on ZnO side and Au on Si / and Au on both sides of the junction) were studied to establish the impact of the Pd-Ag-ZnO catalytic contact on methane sensing properties of such heterojunction sensor. It was observed the device with Pd-Ag (70%) contacts on both sides offered shorter response time (~28sec) and much higher response magnitude (~63%) at 275$^{o}$C compared to the sensor with Au contact both sides (response time ~47 sec and response magnitude ~ 19%) at 300$^{o}$C but it didn't differ much in terms of performance from that of Pd-Ag on ZnO side and Au contact on the Si. (Response time ~31 sec magnitude ~61% at 275$^{o}$C). This emphasizes the importance of the (Pd-Ag (70%)) catalytic contact as well as utility of using such contacts to sensing layer only. Moreover comparison with Pd-Ag (26%) contacts reveals that a higher percentage of Pd in the alloy is much useful in lowering down the operating temperature and improving the sensor parameters like response magnitude ad response/recovery time owing to higher catalytic effect of Pd. The diode parameters and the barrier height were also calculated for all the three ZnO based Schottky devices to justify the experimental results.

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