HIGH SENSITIVITY METHANE SENSOR BY CHEMICALLY DEPOSITED NANOCRYSTALLINE ZNO THIN FILM

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Abstract –Nanocrystalline n-ZnO thin films were deposited on SiO_2-coated (0.45 µm) p type Si substrates (10-20Ω-cm) by a low cost chemical deposition technique to fabricate ZnO-based resistive sensors for methane detection. The nanocrystalline ZnO needle like structures were grown on RCA cleaned p-Si<100> substrates by successive immersion (100-200 times) into a Sodium Zincate bath (0.125M) kept at room temperature and DI water maintained at 90 ^oC . The Sodium Zincate was prepared by reacting Zinc Sulphate and excess Sodium Hydroxide in aqueous solution. The film thickness of 1.5 µm (approx.) for 75 dippings was obtained. The dipping time is 1 second. The annealing was done at a lower temperature (150 ^oC) for 30 minutes in air. Structural characteristics were studied by FESEM and EDAX to indicate the formation of ZnO with vertical orientation. The hexagonal needle like structures of 0.3-0.5µm diameter and 1-1.5µm length were formed. The resistance of the ZnO films in ambient air (zero level for gas sensing) was found to be stable and reproducible after several thermal cyclings. Surface modification with palladium (0.01% $PdCl_2$ for 5 seconds) was done to enhance sensitivity; so that the ZnO thin films can give significant response to target gases at the operating temperature of as low as 130^oC, compared to the normal operating temperature range of 200–400^oC for zinc oxide resistive gas sensors. The planar gold contacts were deposited by vacuum evaporation technique. The device was then tested for its methane sensing property at different operating temperatures (150,175,200,250,300,350^oC) and at 5 different methane concentrations (0.01,0.05,0.1,0.5,1%) taking N_2 as a carrier gas. The response magnitude, response time and recovery time were studied in detail for both Pd modified and unmodified ZnO film. The maximum response of 99.76% and the lowest response time of 39 seconds were obtained at 200^oC for Pd modified sensor. A high sensitivity to methane even at low temperature (130^oC) was observed comparable to those obtained by more sophisticated and expensive deposition process e.g. MOCVD.

Indexterms *:* Nanocrystalline zinc oxide, Methane sensor, Pd modified, Fast response.

I. INTRODUCTION

ZnO is one of the well established gas sensing oxides, which has been extensively studied for detection of inflammable and toxic gases, such as NO_2 [1] CH_4 [2], CO [3] and H_2 [4]. Various forms of nanocrystalline ZnO are available such as, single crystals [5], sol-gel, heterojunction. Thin films of ZnO exhibits a high degree of gas sensitivity because of their high surface to volume ratio, one dimentional vertical alignment and lowering of activation energy for chemisorptions. The vertically oriented ZnO nanostructures as reported are fabricated mostly by the vapour phase transport method at a higher temperature (typically>600°C) [6] , the sol-gel method requires a high annealing temperature (typically>400°C) [7] and low temperature CBD technique still requires a seed layer of ZnO obtained from sol-gel technique to increase the sensitivity [8]. Investigating low temperature fabrication which is necessary for low cost sensors as the power consumption can be kept low, chemical deposition is a useful alternative to the traditional methods for obtaining thin films of pure ZnO. It is of particular interest because of its simplicity, low cost and minimal waste production.

The synthesis of nano particles with different shape and morphology has a strong interest, because the properties depend on their structure, phase, shape, size, and size distribution. In this paper, we report on the fabrication of a low cost, low temperature, high sensitivity methane gas sensor based on a vertically aligned hexagonal nanocrystalline ZnO needle like structure deposited by chemical deposition method on SiO_2-coated p-Si (for CMOS compatibility) and its application as a methane sensor. The sensor study in the resistive mode was performed at different temperatures (150, 200, 250, 300 and 350°C) and at different methane concentrations (0.01, 0.05, 0.1, 0.5and 1%). The response magnitude and the response time as a function of methane gas concentration were studied to achieve the optimum temperature.

Control of catalytic activity of gas sensor material is one of the most commonly used means to enhance the

performances of gas sensors. A significant improvement in terms of response magnitude and response time due to Pd sensitization/modification has been a well observed phenomenon for metal oxide sensors [9]. With nanocrystalline ZnO, Pd sensitization has proven to be a remarkable alternative for lowering operating temperatures and the response time of metal oxide sensors [10]. However many works have been reported so far [11] about dispersing Pd metal

nanoclusters on the thin films leading to electronic sensitization of the metal oxide sensing layer. Our work has focused on to increase the sensitivity to some large extent at a lower temperature through electronic sensitization by uniformly dispersing Pd metal clusters over our sensing layer by a simple dipping technique. The Pd sensitization was found to produce a relatively lower optimum temperature of 200◦C for the maximum response (99.76%) and shorter response time (39 seconds). It was further observed that the sensor could also exhibit a high response magnitude (81.33%) and an acceptable response time (66 seconds) at a temperature as low as 130^{o}C.

II. EXPERIMENTAL

Figure 1 shows the schematic of our typical sensor samples. Undoped nanocrystalline n-ZnO thin films were deposited on SiO_2-coated p-Si substrates (10-20Ω-cm, 400 μm) by a low cost chemical deposition technique to fabricate ZnO-based resistive sensors for methane detection. The SiO_2 was prepared by thermal oxidation of RCA cleaned p-Si<100> wafers (wafer thickness 400μm, resistivity 10-20 Ωcm) in an oxidation furnace (TEMPRESS 201) at 1000^{o}C by 30 min dry oxidation followed by 1 h wet oxidation and again 30 min dry oxidation. The thickness of the SiO_2 layer was 0.45μm. The nanocrystalline ZnO needle like structures were grown on the SiO_2 layer by successive immersion (50-200 times) into a Sodium Zincate (Na_2ZnO_2) bath of 0.125M kept at room temperature and DI water maintained at 90^{o}C . As reported earlier 0.125M concentration has been optimized because at other concentrations the growth rate became erratic and the ZnO deposition was nonuniform(12) the SEM of which is shown in figure 2(a).

The Sodium Zincate was prepared by reacting Zinc Sulphate ($ZnSO_4$,$7H_2O$) and excess Sodium Hydroxide (NaOH) in aqueous solution and was stirred at room temperature[13].

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4 \quad (1)$$

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O \quad (2)$$

$$ZnSO_4 + 4NaOH = Na_2ZnO_2 + Na_2SO_4 + 2H_2O \quad (3)$$

After having a clear transparent homogeneous solution the dipping technique started. The 2cmx1cm silicon substrate is first immersed in sodium zincate bath and then the substrate with a thin layer of sodium zincate is dipped into hot water bath. This leads to the reaction:

$Na_2ZnO_2 + H_2O = ZnO + NaOH$ (4)

The film thickness of 1.5 µm (approx.) was obtained from 75 dippings. The dipping interval is 1 second. ZnO thin films were subsequently annealed at a lower temperature (150^oC) for 30 minutes. It seems that best crystallinity was obtained at this temperature. The sample was also thermally treated at 350^oC. The SEM image is shown in figure 2(b) which clearly illustrates the granular structure of the film was damaged by high temperature thermal treatment.

The hexagonal needle like structures of 0.3-0.5µm diameter and 01-1.5µm length were formed with good coverage over the substrate. The resistance of the ZnO films in ambient air (zero level for gas sensing) was found to be stable and reproducible after several thermal cycling.

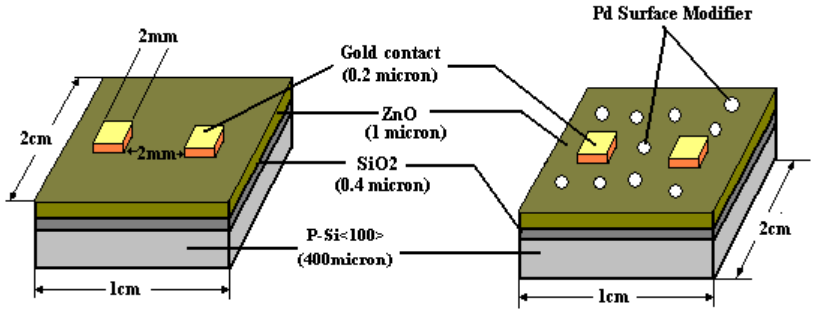


Figure 1. Schematic of the unmodified and Pd modified sensor structure

a.Surface modification by palladium

Noble metal additives (Pd,Pt,Rh etc.) with high-effective oxidation catalytic activity can be used to enhance the sensitivity of pure metal oxides due to the “spillover effect” The very high surface to volume ratio has attracted much attention in the application of gas sensors. High surface areas make them excellent supporting materials, which can obtain well-dispersed gas sensor materials or catalysts. Here the surface of porous ZnO thin films was Pd sensitized by single dipping technique. The dipping was done in an aqueous solution of 0.01(M) $PdCl_2$ for 5s. After Single dipping the film was withdrawn from the solution and the water was allowed to evaporate leaving behind a coating of $PdCl_2$ by15 minutes annealing at 110^oC.

When the sample is dipped in $PdCl_2$ solution, the n type ZnO selectively adsorbs Pd^{2+} ions.[13] The Pd^{++} ions are then converted to Pd by having two electrons from the ZnO . The chemical reaction is shown below [14]

$Pd^{2+} + O = Pd{:}O$ (5)

Pd present on the surface acts as a very good adsorption center for H (formed by stepwise dissociation of methane). Also as weakly bound Pd:O on the metal oxide surface is reduced by hydrogen to produce H_2O ; electrons are released which help lower the resistance of the sensor considerably. Pd may also have an impact on reducing the activation energy required for dissociation of methane thus lowering the operating temperature. [15]. It has also been observed that depending upon the material, surface condition, morphology there exists an optimum temperature for gas sensing by such Pd sensitized and also Pd unsensitized metal oxide surfaces .

III. RESULTS & DISCUSSIONS

For gas sensing we used a setup consisting of a cylindrical testing chamber made of glass (length 25cm and dia. 3.5cm). The sensor sample was inserted in the central portion of the cylinder from one side which was then heated with a resistive heating coil providing about 7 cm of heating zone (temperature maintained to an accuracy of $\pm 1^{o}$C). The sensor sample of 2cmx1cm dimension with 2mmx2mm gold contact pads (at 2mm separation) were deposited on top of the sensing layer; we used fine conducting wires as the connecting leads. IOLAR grade N_2 was used as the carrier gas for ultra pure methane gas which is mixed in a proportion inside a mixing chamber. The gas flow and mixing ratio were precisely monitored and controlled with the help of mass flow controller (MFC) (Alicat scientific, M-50SCCM-D) for methane and a needle valve and mass flow meter(MFM) (Alicat scientific, M-1000SCCM-D) for N_2. The homogeneous mixture carrying the desired percentage of the target gas was fed into the chamber with a flexible PVC pipe. During the testing the gas pressure on the sensor was 1atm. For sensor resistance measurement the electrodes are connected to an Agilent U1252A Multimeter with Agilent GUI Data logging software (v2.0).

a. FESEM and EDS

The samples prepared were characterized with Field Emission Scanning Electron Microscopy (FESEM; JEOL, JSM-6700F used emitter voltage = 5 kV and emitter current =10μA), Energy Dispersive X-ray Scattering (EDS; Jeol JSM-6X60La used emitter voltage = 20 kV and emitter current = 20μA). Figure 3(a) and 3(b) shows the FESEM images of the sensitized and the unsensitized samples respectively, annealed at 150°C for 30 minutes and 3(c) and 3(d) shows the

EDS analysis of the ZnO film for both the cases. The EDS analysis reveals that the Pd unmodified sample had (by mass) 83.19% ZnO and 16.01% SiO_2. The overall mass percentage of Zn was 66.83%. On the other hand, the sensitized sample had (by mass) 69.47% ZnO and 29.68% SiO_2 and the overall mass percentage of Zn were 55.81%. The sample also showed the presence of 0.74% Pd by mass. It is very much prominent the tiny Pd metal nanoclusters which are spread out over the sample from FESEM image. Dispersed Pd^{2+} ions want to attain charge neutrality by forming weak bond with O by adsorbtion (to form O^- species) from the ambient. Such a loosely bound Pd:O is shown as the 0.86% (by mass) PdO .

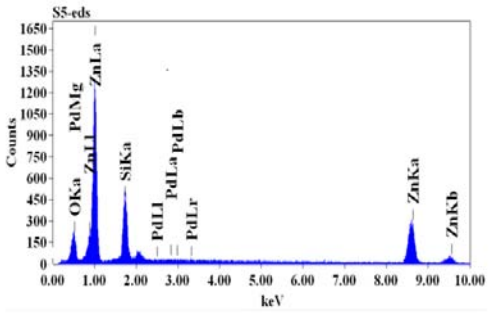


(a) (b)

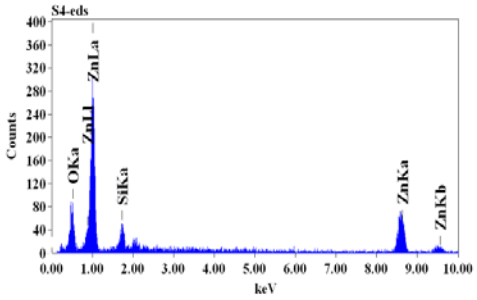
Figure 2. (a and b) FESEM images of crystal growth with 0.125M solution and a separate sample annealed at 350 ^oC respectively.



(a) (b)



Ele...	Cl...	(keV)	mass%	Error%	At%	Comp...	mass%
O			29.57				
Si K		1.739	13.87	0.47	36.46	SiO2	29.68
Zn K		8.630	55.81	1.21	63.02	ZnO	69.47
Pd L*		2.838	0.74	0.54	0.52	PdO	0.86
Total			100.00		100.00		100.00



Ele...	Cl...	(keV)	mass%	Error%	At%	Comp...	mass%	Cation
O			25.31					
Si K		1.739	7.86	0.87	21.49	SiO2	16.81	4.24
Zn K		8.630	66.83	2.03	78.51	ZnO	83.19	15.51
Total			100.00		100.00		100.00	19.76

(c) (d)

Figure 3. (a and b) FESEM images and (c and d) EDS spectra of Pd-modified and unmodified ZnO thin films respectively.

The sensors were tested in resistive mode by measuring the resistance of the sensor with respect to time while charging the target gas i.e. methane into the chamber. We defined Response magnitude (S) to be:

$$S = (R_a - R_g)/R_a \qquad RM = (R_a - R_g)/R_a \times 100\%$$

where R_a indicates the sensor sample resistance in air (i.e. at 0% methane concentration) and R_g is the resistance at a given concentration of the target gas (methane). Before starting the sensing the entire setup is flushed with IOLAR grade N_2 for 15 minutes. We performed the testing at 5 different methane concentrations (0.01,0.05,0.1,0.5,1% by mass) taking N_2 as a carrier gas at different temperatures (150, 175, 200, 250, 300 and 350 ◦C). The sensor resistance remains in the range of about 6.5KΩ to 3.5MΩ depending on the surface sensitization and temperature.

b. Gas sensing

Gas sensor measurement setup is shown in figure 4. Dynamic response curves of Pd unsensitized and Pd-sensitized sensor at optimum temperature (300^{o}C and 200^{o}C respectively) for different methane concentrations are shown in figure 5(a) and (b). When O_2 molecules are adsorbed on the surface of metal oxides, they would extract electrons from the conduction band and trap the electrons at the surface in the form of ions. When the sample is exposed to methane, due to stepwise dissociation of methane at an optimum temperature H^+ ions are produced which then

react with the O^- ions to produce water molecules and this decrease of the number of surface O^- ions, the thickness of space-charge layer decreases. Then the Schottky barrier between two grains is lowered and it would be easy for electrons to conduct in sensing layers through different grains. It means when the sample is exposed to methane, resistance is decreased due to free electron release from the surface but when the gas is cut off then the resistance is increased and it reaches to its baseline value where nearly all the gas molecules are released from the ZnO surface. We observed a fluctuation in resistance, which could be associated to the variation of atmospheric room conditions. We know that the temperature has the influence on the adsorption rate. Adsorption of methane molecule on the ZnO surface increases with increase in temperature as a result with increase in methane concentration much more free electrons are released from the surface and thus lowering barrier height and hence the resistance. Figure 6(a) and (b) shows the variation of response magnitude as a function of temperature both for as deposited and Pd modified sensors respectively. Variation of response magnitude with methane concentration at different temperatures is shown in figure 7(a) and (b) respectively. For concentrations 0.01% to 1.0%, the Pd unmodified sensor showed a maximum response at 300°C. It is well known that there exists a strong influence of temperature on the adsorptive and catalytic behavior of Pd-ZnO thin films [16] and pore structure collapses at high temperature [17]. For Pd modified sensors the maximum response is obtained at around 200°C which is lower than that of the pure ZnO sensor (300 °C). Weakly bound Pd:O on the metal oxide surface is reduced by hydrogen to produce H_2O; electrons are released which help to lower the resistance of the sensor considerably. As the Pd modified surface offered higher amount of adsorption sites the modified structure showed appreciable response to a very lower (0.01%) concentrations as well as to quite high concentration like 1% methane. Table1 and Table2 represents the response magnitude, response time and recovery time at five different gas concentrations and at different operating temperatures for unmodified and Pd modified ZnO sensor respectively. As revealed from the Table1, for unmodified case the sensor showed no response to the lower temperature (150^{o}C). As the temperature increases response also increases.

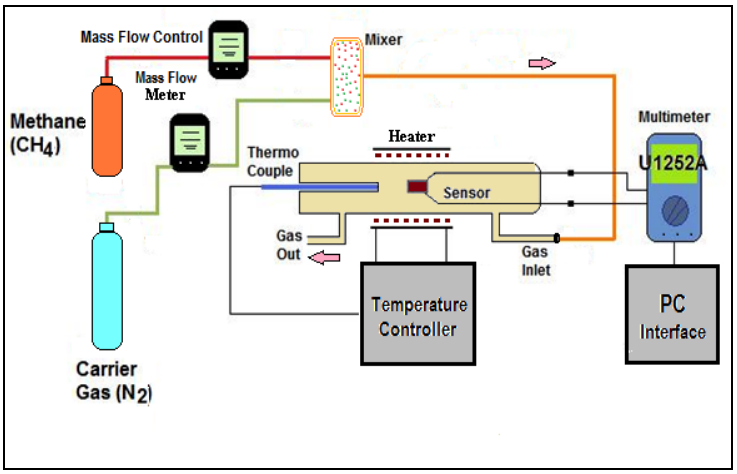
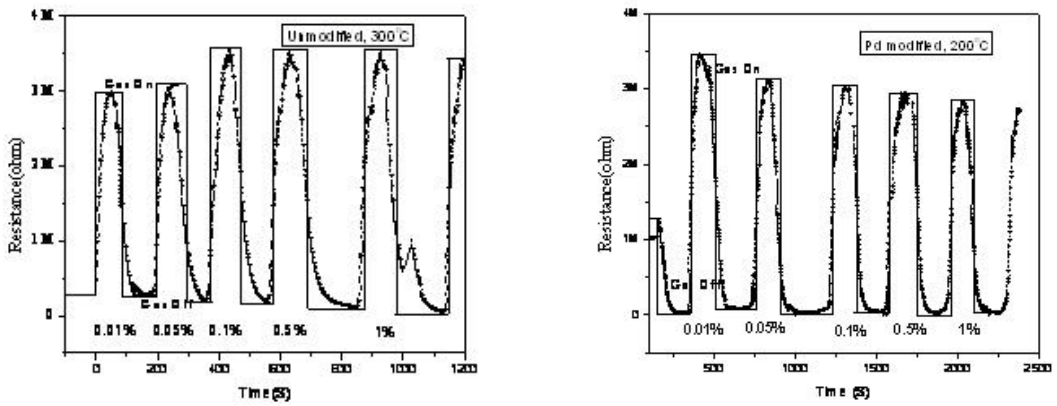
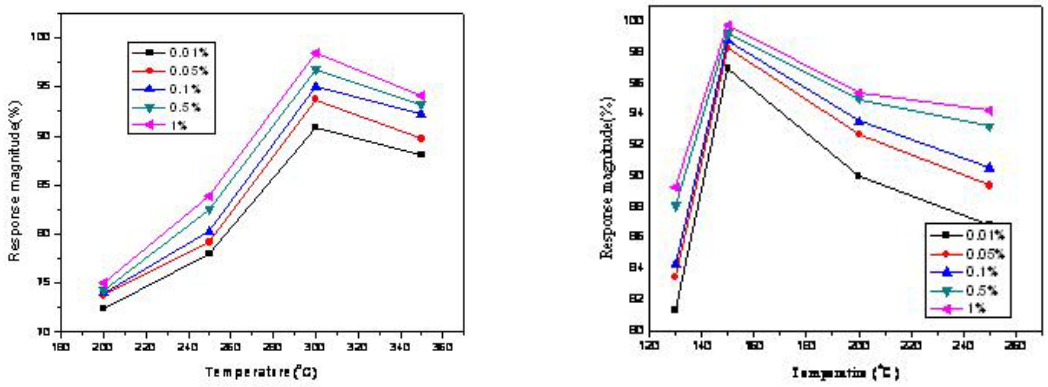


Figure4. Schematic of the gas sensor measurement setup



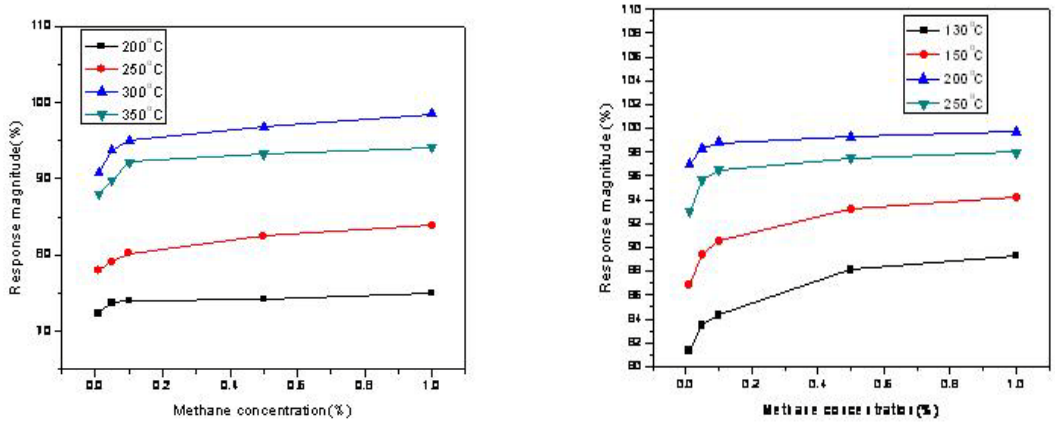
(a) (b)

Figure 5. Dynamic response characteristics of (a) unmodified and (b) Pd modified ZnO sensor for different methane concentrations



(a) (b)

Figure 6. Response magnitude of (a) unmodified and (b) Pd modified ZnO sensor as a function of temperatures for different methane concentrations



(a) (b)

Figure 7. Response magnitude of (a) unmodified and (b) Pd modified ZnO sensor as a function of methane concentrations for different temperatures.

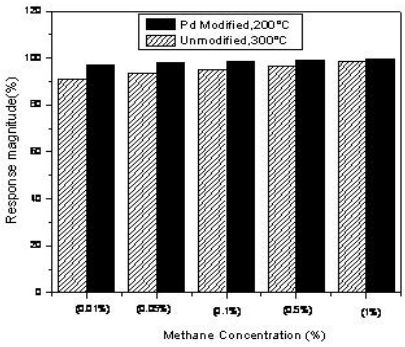
Table 1: Pd unsensitized sensors at different operating temperatures and for different methane concentrations

Operating Temp.(°C)	**Methane Conc(%)**	**Response Magnitude (%)**	**Response Time (S)**	**Recovery Time (S)**
150 unsensitized	No response			
200 unsensitized	0.01	72.35	96	106
	0.05	73.75	84	109
	0.1	74	75	116
	0.5	74.28	66	126
	1	75	61	134
250 unsensitized	0.01	78.01	87	76
	0.05	79.17	79	84
	0.1	80.24	64	91
	0.5	82.5	58	99
	1	83.9	49	101
300 unsensitized	0.01	90.84	52	55
	0.05	93.71	50	58
	0.1	95.0	48	59
	0.5	96.74	44	64
	1	98.48	40	71
350 unsensitized	0.01	88.05	66	85
	0.05	89.75	63	92
	0.1	92.2	57	102
	0.5	93.23	48	106
	1	94.1	39	117

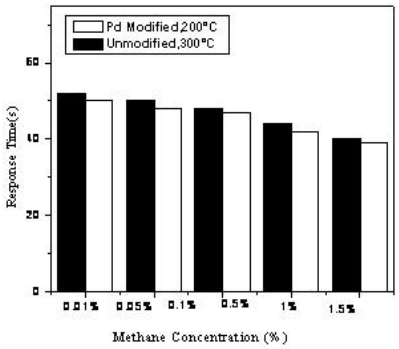
Table 2: Pd sensitized sensors at different operating temperatures and for different methane concentrations

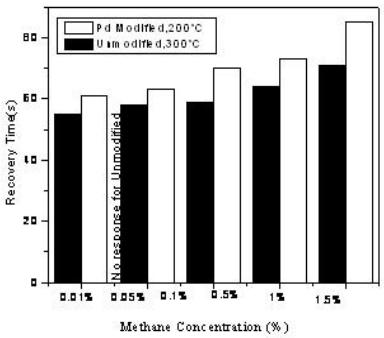
OperatingTemp.(^{o}C)	**MethaneConc(%)**	**ResponseMagnitude(%)**	**Response Time (S)**	**Recovery Time (S)**
130 sensitized	0.01	81.33	85	92
	0.05	83.45	79	96
	0.1	84.3	74	104
	0.5	88.1	68	112
	1	89.3	66	121
150 sensitized	0.01	86.84	72	71
	0.05	89.38	65	77
	0.1	90.52	61	82
	0.5	93.23	57	89
	1	94.24	54	96
200 sensitized	0.01	97	50	61
	0.05	98.28	48	63
	0.1	98.8	47	70
	0.5	99.26	42	73
	1	99.76	39	85
250 sensitized	0.01	90	69	68
	0.05	92.68	62	75
	0.1	93.54	58	84
	0.5	95	54	91
	1	95.34	51	93

Figures 8(a), (b) and (c) show the bar chart of the response magnitude, response time and recovery time for this sensor without and with Pd modification at the optimum temperature and at five different methane concentrations. For unmodified case the maximum response was 98.48% and the minimum response time and recovery time were found to be 40s and 71s in the presence of 1.0 % methane and at 300°C. For Pd modified sensor with the same concentration of methane the maximum response of 99.76 % was obtained at 200°C, the minimum response and recovery time were found to be 39s and 85s (for 1% methane), respectively. The grain size becomes comparable to twice the Debye length, a space-charge layer can cover the whole crystallite as mentioned in [18] and it allows achievement of maximum sensor response in this case.



(a)





(b) (c)

Figure 8. Bar diagram showing (a) response magnitude (b) response time (c) recovery time of unmodified and Pd modified ZnO sensor for five different methane concentrations.

The reactivity and sensitivity of a nanostructure can be tailored by controlling the shape, as it will determine the crystallographic facets exposed on the surface of a nanocrystal and therefore the number of atoms located at the edges or corners [19]. In our work, uniform hexagonal ZnO nanocrystals were prepared and gas response exposure to CH_4 was tested . The results indicated that the 6-faceted structure has a higher sensitivity than those produced by sol-gel or other technique, due to a larger active surface area of each facets, which can provide more active space for the interaction between ZnO and target gases and also adsorb more oxygen or hydrogen to promote the reaction between hydrogen and the surface adsorbed oxygen. Probably this is the reason of giving high response magnitude in the Pd unmodified sensor with nearly equal response time for both the cases (i.e. as deposited and Pd modified) in this work. Besides the activation of the crystallographic facets exposure to target gases, high surface to volume ratio is also crucial as mentioned above. However, high surface to volume ratio can be obtained not only by reducing grain size, but also by highly-ordered porous structure.

IV. CONCLUSION

ZnO needle like structures were grown by a simple low cost chemical deposition method on SiO_2/Si substrate to fabricate methane sensor. The fabricated sensor was Pd sensitized by simple dipping technique in order to study the effect on response magnitude, response time and recovery time. Gold contact electrodes (planar structure) were evaporated on the sensing layer. Sensor study reveals that Pd sensitized thin film (1.5μm) can act as a very high sensitivity methane sensor with operating temperature of 200^{o}C giving the best results displaying 97% response with a response time of 50 s for much lower (0.01%) methane concentration. The presence of Pd nanocluster in the sensing layer lowers the operating temperature as low as 130^{o}C with a sufficiently high response magnitude (81.33% at 0.01% methane) and for the higher concentrations (0.5%-1.0%) the response time was shortened to 66s for 1% methane concentrations with response magnitude 89.3%. Smaller grain size in the nanocrystalline material lowers the activation energy and the presence of dispersed Pd nanocluster over the ZnO surface further reduced the activation energy. This is the reason of lowering the operating temperature of the Pd modified sensor. For future development it has to be shown that change in the proportions of single material from the wide range of sensor materials with very different sensing characteristics.

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