Effect of Catalytic Contact on Methane Sensitivity using Chemically Deposited Zinc Oxide Thin Film

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ABSTRACT
Nanocrystalline n type ZnO thin films were deposited on SiO_2-coated (0.4 µm) 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 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 0.5-1 µm (approx.) for 100 dippings was obtained. The dipping time is 1-2 seconds. Air annealing was done at a lower temperature of 150^oC for 30 minutes. Structural characteristics were studied by FESEM and EDS to indicate the formation of ZnO. The hexagonal needle like structures of 0.3-0.5µm diameter and 0.5-1µm 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. Two types of planar contacts (Au and Pd-Ag) were deposited by vacuum evaporation technique and the device was then tested for its methane sensing property at different operating temperatures (150 to 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. Pd is a far better oxygen dissociation catalyst. A high sensitivity to methane even at low temperature (150^oC) was observed with Pd-Ag (70%) contact comparable to those obtained by pure Au contact.

Keywords
Chemical deposition; Nanocrystalline zinc oxide; Methane sensor; Pd-Ag (70%) contact; High sensityvity

1. INTRODUCTION
So far various types of semiconducting metal oxides were reported as a sensing material in gas sensors, such as ZnO, SnO_2, TiO_2 and so on. Due to the natural non-stoichiometric properties, free electrons generated from oxygen vacancies generated the change in conductivity when the composition of the surrounding atmosphere is altered [1]. ZnO is one of the promising materials for gas sensor application, and during the last years many works on the structural, electrical properties and sensing characteristics of ZnO thin films has been studied. It was reported by different authors that ZnO based thin and thick films were both sensitive to a broad range of oxidizing or reducing gases such as H_2[2], CH_4[3] and CO. Most of the metal oxide gas sensors suffer from fluctuation from its base value and lack of selectivity which has to be solved by taking numbers of different strategies such as the sensor's transient response analysis for gas detection.
In addition to the above mentioned strategies, the modification of the metal oxide surface layer by adding small amount of noble metals (Au, Pt, Pd and Ag), recently explored a promising field in the area of sensors selectivity improvement. Besides the high surface to volume ratio, activation energy and the crystallographic facets exposure to target gases, is also a crucial point. The noble metals can be incorporated in the active layer as (i) catalytic electrode contact and/or (ii) dispersed phase on the semiconducting oxide surface. Here we are utilizing the effect of noble metal catalytic contact to increase the sensitivity to the target gas.
The main objective of our work was the understanding of the mechanisms which explain the activation of ZnO thin film sensors by incorporating noble metal catalytic contact. For that, two types of metal contacts have been chosen Pd-Ag(70%) and Au (99.99%) and their effect on the sensor sensitivity towards methane were studied. In earlier reports[4] Pd-Ag (26%) alloy were used for the catalytic contacts but in this report we present a different composition Pd-Ag (70%) alloy to investigate the impact on the sensing property. The responses increase and reach their maximums at a certain temperature, and then decreased rapidly with increasing the temperature. Studies on methane sensing properties of a zinc oxide based sensor with catalytic Pd-Ag contact proven a promising effect over Au contact [5]. With nanocrystalline ZnO, Pd-Ag catalytic contact has proven to be a remarkable alternative for lowering operating temperatures and the response time of metal oxide sensors as it shows a very porous flaky nature for Pd-Ag(70%) metal while the Au contacts are less porous[5]. This porous nature also takes a very significant role regarding the chemisorptions kinetics of methane. The Pd-Ag catalytic contact was found to produce a relatively lower optimum temperature of 180◦C for the maximum response (99.31%) and short response time (38s).

2. EXPERIMENTAL
The schematic of the sensor configuration is shown in Fig. 1. 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. It is of prime importance that variables such as temperature, concentration and rate of dipping are well controlled.The SiO_2/Si substrates were 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^oC by 30 min dryoxidation 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 RCA cleaned p-Si<100> substrates 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^oC . As reported earlier 0.125M concentration has been optimized because at other concentrations the growth rate became erratic and the ZnO deposition was nonuniform (6). The Sodium Zincate was prepared by reacting Zinc Sulphate (ZnSO4,7H2O) and excess Sodium Hydroxide

(NaOH) in aqueous solution and was stirred at room temperature[7].

$$Zn(SO_4) + 2NaOH = Zn(OH)_2 + Na_2SO_4 \quad (1)$$
$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O \quad (2)$$
$$ZnSO_4 + 4NaOH = Na_2ZnO_2 + Na_2SO_4 + 2H_2O \quad (3)$$

After having a clear transparent homogeneous solution the dipping technique started. The 2cmx2cm 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. Here the reaction started:

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

The film thickness of 1 µm (approx.) was obtained from 70 dippings. The dipping interval is 1 second. ZnO thin films were subsequently annealed at a lower temperature (150^{o}C) for 30 minutes. Figure 1(a) and (b) shows the schematic of our typical sensor sample. The hexagonal needle like structures of 0.3-0.5µm diameter and 0.5-1µm length were formed with a 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. Two samples under same atmospheric conditions were prepared. Au and Pd-Ag (70%) were deposited on the two separate samples by an e-beam deposition method (10^{-6} mbar) using Al metal masks. The contact area was kept 2mm×2mm in both the cases.

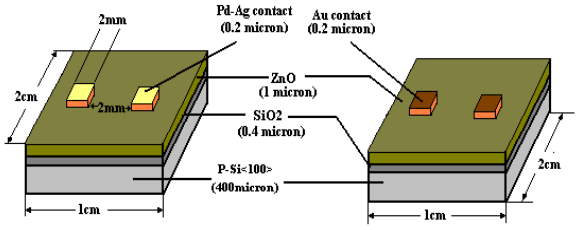
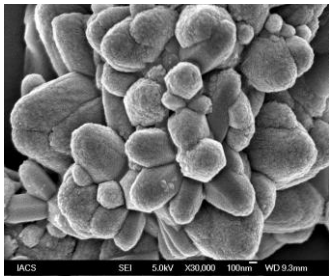
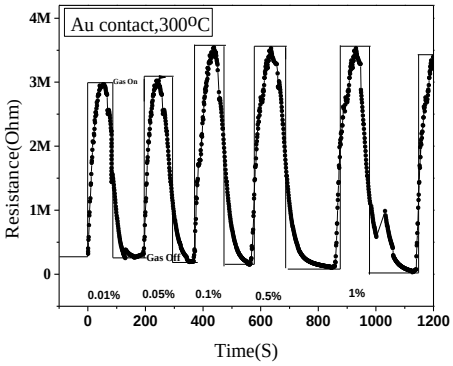


Fig. 1. Schematic of the Au contact and Pd-Ag contact sensor structure

3. RESULTS & DISCUSSIUONS

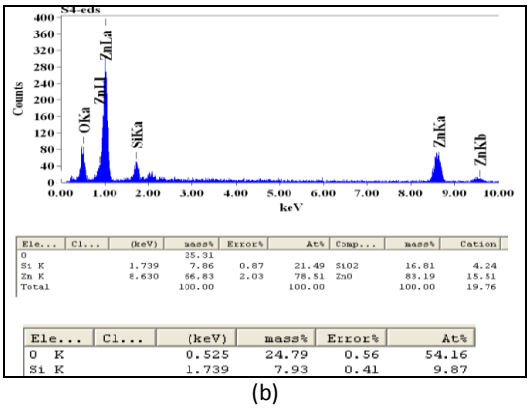
The samples prepared were characterized with Field Emission Scanning Electron Microscopy (FESEM; JEOL, JSM-6700F used emitter voltage = 5 kV and emitter current =10µA), Energy Dispersive X-ray Scattering (EDS; Jeol JSM-6X60La used emitter voltage = 20 kV and emitter current = 20µA). Figure 3(a) shows the FESEM images sample, annealed at 200˚C for 15 minutes and 2(c) shows the EDS analysis of the ZnO film. The EDS analysis reveals that the sample had (by mass) 83.19% ZnO and 16.01% SiO_2. The overall mass percentage of Zn was 66.83%. For gas sensing we used a setup consisting of a cylindrical glass chamber (length 25cm and dia 3.5cm). The sensor sample was placed in the central portion of the cylinder which was heated with a resistive heating coil (temperature maintained to an accuracy of ±1^{o}C). The sensor samples of 2cmx1cm dimensions with 2mmx2mm Gold/Pd-Ag contact pads (at 2mm separation) fabricated 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 which is mixed in proportion in a chamber followed by a mixing coil. 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. During the testing the gas pressure on the sensor was 1atm. For sensor resistance measurements the electrodes are connected to an Agilent U1252A Multimeter with Agilent GUI Data logging software (ver. 2.0). 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 (of specific concentration) into the chamber. We defined sensitivity (S) as: S = (Ra – Rg) / Ra. 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 for15 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, 200, 250, 300 and 350˚C). The sensor resistance remains in the range of about 5KΩ to 3.5MΩ depending on the type of contact and temperature.





(a)

Fig.2. (a) FESEM micrograph of as-deposited ZnO thin films annealed at 150^{o}C for 30 minutes.

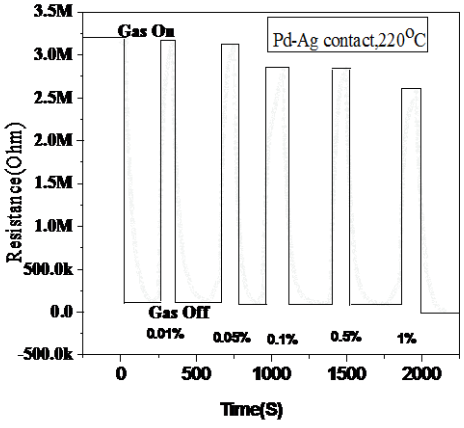


(b)

Fig.2. (b) EDX spectra of ZnO thin films.

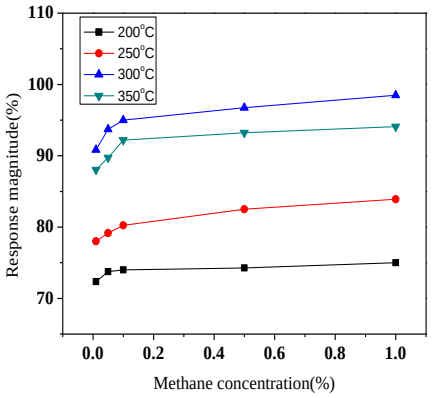
4. GAS SENSING

Dynamic response curves of chemically deposited ZnO based sensor for Au-contact and Pd-Ag contact sensor at optimum operating temperature (300°C and 220°C respectively) for different methane concentrations are shown in Fig 3(a) and (b). It shows 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. Some spikes are there in response curve, which may be due to the variation of atmospheric 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 hence the sensitivity increases. Fig 5(a) and (b) shows the variation of response magnitude as a function of temperature both for Au contact and Pd-Ag catalytic contact respectively. Variation of response magnitude with methane concentration at different temperatures is shown in figure 6(a) and (b) respectively. It was observed that the Pd-Ag contact is more efficient for sensing lower concentrations of methane. For concentrations 0.01% to 1.0%, the Au contact showed a maximum response at 300°C. In contrast, it is well known that there exists a strong influence of temperature on the adsorptive and catalytic behavior of Pd-ZnO thin films [8]. For Pd -Ag catalytic contact the maximum response is obtained at around 220°C. Table1 and Table2 represents the response magnitude, response time and recovery time at five different gas concentrations and at different operating temperatures for Au contact and Pd-Ag contact respectively. It was observed that for Au contact there is no response to the lower temperature (150°C). As the temperature increases response also increases.

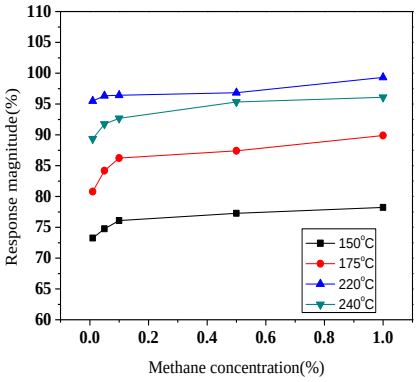


(b)

Fig. 3. Transient response characteristics with (a) Au contact (b) Pd-Ag contact

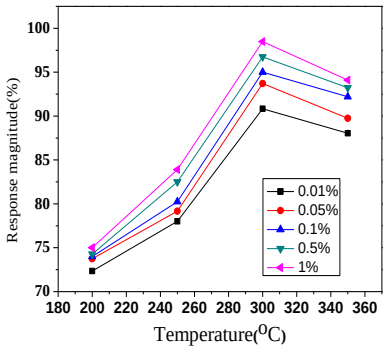


(a)

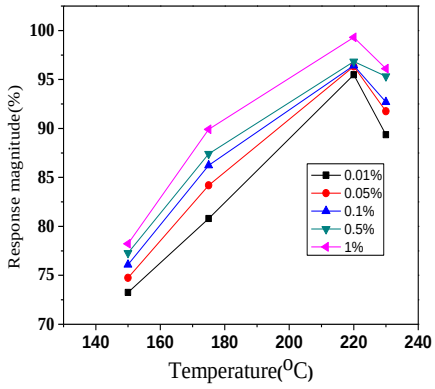


(b)

Fig.4. Response magnitude of (a) Au contact (300°C) and (b) Pd-Ag contact (220°C) as a function of methane concentrations for different temperatures.



(a)



(b)

Fig.5. Response magnitude for (a) Au contact (300°C) and (b) Pd-Ag contact (220°C) as a function of temperatures for different methane concentrations

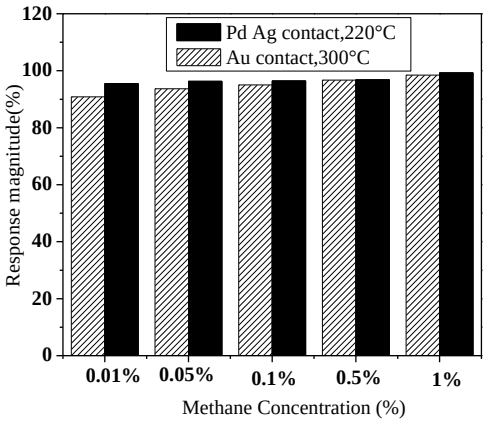
Table 1: Au contact at optimum temperature with different methane concentrations

Au – contact Temperature (°C)	Methane Conc(%)	Response Magnitude (%)	Response Time (S)	Recovery Time (S)
300	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

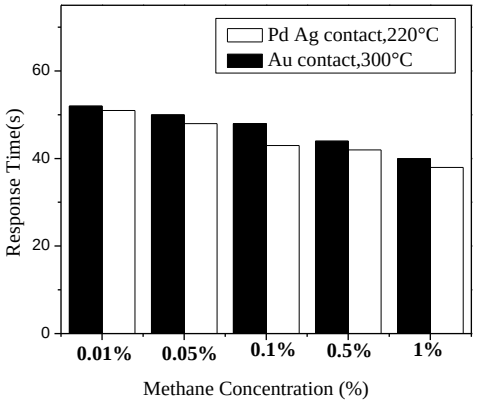
Table 2: Pd-Ag contact at optimum temperature with different methane concentrations

Pd-Ag contact Temperature (°C)	Methane Conc(%)	Response Magnitude (%)	Response Time (S)	Recovery Time (S)
220	0.01	95.48	51	55
	0.05	96.33	48	70
	0.1	96.42	43	77
	0.5	96.84	42	90
	1	99.31	38	111

Figs. 6 (a), (b) and (c) show the bar chart of the response magnitude, response time and recovery time for Au contact and Pd-Ag contact at the optimum temperature and at five different methane concentrations. For Au contact the maximum response was 98.48% and the minimum response time and recovery time were found to be 33 s and 71s in the presence of 1.0 % methane and at 300°C. For Pd-Ag contact, with the same concentration of methane the maximum response of 99.31 % was obtained at 220°C, the minimum response and maximum recovery time were found to be 38s and 111s (in 1.0 % methane), respectively after which the sensitivity decreases.



(a)



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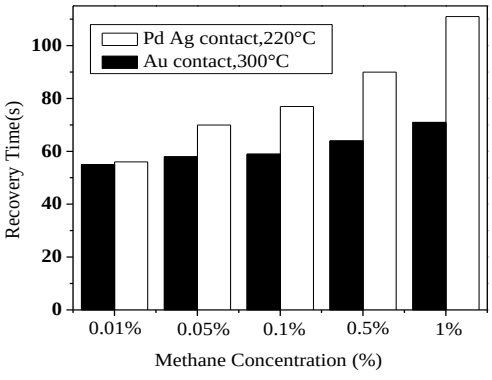

(c)

Fig.6. Bar diagram showing (a) response magnitude (b) response time (c) recovery time for (a) Au contact (300°C) and (b) Pd-Ag contact (220°C) ZnO sensor for five different methane concentration

The reactivity and sensitivity of a nanostructure can be altered by varying the shape and size [9]. In our work, uniform hexagonal ZnO nanocrystals were prepared and gas response exposure to CH_4 was tested. The results indicate that the 6-faceted structure has a higher sensitivity due to a larger active surface area of each facet, 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 this chemically deposited ZnO sensor.

As suggested by recent publications [10] adsorption and desorption rates of CH_4 on ZnO surface (with or without sensitization) determine the optimum value of the operating temperature for gas sensor applications. The adsorption rate of methane molecules on the ZnO surface increases with increasing temperature and ultimately peaks at a certain temperature. At the same time rate of desorption of the gas molecules also increases with increasing temperature which at some optimum temperature becomes greater than the rate of adsorption as a result sensitivity decreases. Based on these we can attempt a qualitative explanation regarding the temperature dependent response behavior [Fig. 5(a)-(b) & Fig. 6(a)-(b)] of our sensor which is given in a compact form in Table. 1&2.

5. 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 sensors were tested with two types of contact (Au and Pd Ag) to study the effect on response magnitude, response time and recovery time. Sensor study reveals that Pd Ag contact (0.5μm) can act as a very high sensitivity methane sensor with operating temperature of 150^{o}C giving the best results displaying 73.25% response with a response time of ~88s and recovery time of ~92s for much lower (0.01%) methane concentration. Smaller grain size in the nanocrystalline material lowers the activation energy and the presence of Pd in the contact layer on top of the ZnO surface further reduced the activation energy. This is the reason of lowering the operating temperature from the Pd –Ag contact ZnO sensor. For future development there exists scope of the new sensor material, trying out new contact materials and applying different sensitization methods to improve response time and quantitative response to methane.

5. ACKNOWLEDGMENTS

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