Chapter 4

Response of Gridded Gate $Pt/SiO_2/Si$ MOS Sensor for H_2, NH_3, CH_4 and H_2S

This chapter describes the results of C-V and G-V characteristics of fabricated gridded gate $Pt/SiO_2/Si$ MOS capacitor sensor, upon exposure to hydrogen, ammonia, methane and hydrogen sulphide gases for various frequencies, at room temperature. Interface properties of the MOS sensor have been studied as a function of gas concentration and measurement frequency. The goal of this study was to investigate the sensing behavior towards test gases (H_2, NH_3, CH_4 and H_2S), effect of measurement frequency and gas concentration on sensitivity, and sensing mechanism of gridded gate MOS sensor**.**

4.1 Introduction

Metal-insulator-semiconductor (MIS) structures are well known for H_2 gas sensing since the first MIS ($Pd/SiO_2/Si$) structure fabricated by Lundstrom *et al.* in 1975 [Lundstrom *et al.* (1975(a&b))]. These MIS sensors are based on the change in the flat band voltage with change in device environment and also a lot of studies are available on such structures as discussed earlier in chapter 1 with different thicknesses of metal and oxide (SiO_2) films from 100 to 1000 Å and 30-1000 Å, respectively. The sensitivity of these Si based H_2 sensors is governed by Fermi level pinning effect which is caused by the formation of Palladium Silicide which significantly depends on the thickness of oxide layer and hence with increase of oxide layer the sensitivity of the device decreases. Therefore, Si-based gas sensors are preferably fabricated with a thin oxide layer [Lundstrom (1981); Poteat (1981); Fang *et al.* (1990); Nie and Nannichi (1991); Kuliev *et al.*(1983)]. Kobayashi *et al.* [Kobayashi *et al*. (1995)] fabricated a similar type of structure ($Pt/SiO_2/Si$) with Platinum (Pt) as metal layer and a voltage shift (ΔV) was observed with H_2 exposure. The sensitivity of their structure was found to depend on three processes: (a) decrease in the effective work function of Pt, (b) internal field dependent movement of H_2 ions

in the SiO_2 layer and (c) formation of the interface states. Beside MIS structure, metal-oxide-semiconductor (MOS) structures are also commonly used for H_2 sensors and in this type of sensor the mechanism involved has three basic steps: (i) dissociation of molecular hydrogen in atomic form at metal surface, (ii) diffusion of atomic hydrogen in metallic gate and (iii) adsorption of H_2 atoms at metal oxide interface which induces polarization effect and recorded as a sensing response through electrical measurements [Ekedahl *et al*. (1998)]. The metallic gates associated with the MOS devices may be of continuous or discontinuous type. The continuous metallic gates hinder the diffusability of gas and hence lower down the sensitivity of the device significantly. Therefore, an alternative gridded (discontinuous) approach is proposed by some researchers [Filippini *et al.* (2003)]. In such gridded techniques an alternative path is provided for enhancing the diffusibility of gas atoms/molecules and gas sensing mechanism can be attributed to the following: (i) change in capacitive couple potential of metal to semiconductor surface through bare oxide, (ii) direct adsorption of dissociated dipole, (iii) spill over of gas molecules from catalytic metal to the SiO_2 with generation of charged particles [Lundstrom *et al*. (1981/82)]. In such discontinuous/gridded metal gate structures, the sensitivity of device is incredibly enhanced towards several H_2 containing gases like NH_3, H_2S etc. [Lundstrom *et al.* (1989)]. Yadava *et al*. (1990) observed ~47% sensitivity towards H_2 in Pd/TiO_2/Si MOS capacitor in N_2 ambient atmosphere. In another study by Pandey *et al.* [Pandey *et al*. (2009(a))] on Pd/SiO_2/Si MOS capacitor based structure observed ~73.3% sensitivity towards H_2 at room temperature. Pandey *et al.* [Pandey *et al*. (2009(b))] has also observed the change in sensitivity (73.3 to 74.4%) after RF and microwave oxygen plasma treatment of Pd/SiO_2/Si MOS capacitor sensor. Harris reported Pt/TiO_2/Si MOS sensor for H_2 detection. The detection of H_2 was based on change in conductance of TiO_2 [Harris (1980)].

This chapter deals with the C-V, G-V response of gridded gate Pt/SiO_2/Si MOS sensor for various concentrations of test gases (H_2, NH_3 and CH_4) at room temperature (~27 ^oC) and for H_2S at 120 ^oC in air atmosphere. The C-V and G-V characteristics for H_2 and NH_3 were taken at three different frequencies 15 KHz, 25 KHz, and 50 KHz at room temperature. The same measurements were carried for CH_4 and H_2S at 25 KHz at room temperature and 120 ^oC, respectively. All the

measurements are carried out in air. The interface trap charge density (N_{it}) has been extracted from the G-V curve using a bias scan conductance method at different frequency (15 KHz, 25 KHz and 50 KHz) for H_2 and NH_3 and for CH_4 and NH_3 at 25 KHz. N_{it} was found to be decrease with increasing concentrations of various gases. The sensor shows better sensitivity (~90%) towards H_2 as compared to other gases (NH_3, H_2S and CH_4) at lower frequency (15 KHz). Moreover, the sensor is also useful for detecting a very low concentrations of NH_3 (25 ppm), CH_4 (50 ppm) at room temperature and H_2S (10 ppm) at 120 ^oC.

4.2 Experimental Details

4.2.1 Device Fabrication

The gridded Pt gate MOS capacitor sensor was fabricated on 3" P type <100> (1-6 Ω-cm) Si wafer. For fabrication of Pt/SiO_2/Si MOS capacitor, the wafer was thoroughly cleaned using standard technological cleaning procedures used in silicon technology as described in section 3.4.2 of Chapter 3. The SiO_2 layer (about 100 Å) was grown by dry thermal oxidation of silicon wafer in the oxidation furnace (the detailed procedure is mentioned in Chapter 3, section 3.4.3). Subsequently, photolithography technique was used for retaining front side oxide and removing back side oxide (as mentioned in section 3.4.4). After that a platinum film of average thickness 350 Å has been deposited on front face of silicon wafer by thermal evaporation method. Details of fabrication steps have been described in section 3.4 of Chapter 3. 3-D structure of gridded gate Pt/SiO_2/Si MOS sensor is shown in Fig. 3.5 of Chapter 3.

4.2.2 Surface Characterization of Device

The microstructural analysis was carried out by SEM (Quanta 200 F) and contact mode AFM (model no.-NSE, Nanoscope E Digital Instrument Inc., U.S.A.). The surface morphology of the deposited Pt film has been investigated through SEM study (shown in Fig. 4.1). It is revealed from the Fig.4.1 that Pt microstructures are uniformly distributed throughout the film surface. Moreover, the film surface comprising cracks and microporous structures which may lead to improved sensing behaviour of the device. Further, the surface morphology and porous nature of the deposited Pt gate structure has been investigated through AFM study (Fig.4.2). AFM study reveals the microporous nature of the fabricated device metal gate layer. The

surface roughness of deposited Pt film also evaluated from AFM micrograph and the rms value of surface roughness was found to be 2.70 nm.

4.2.3 Electrical Characterization

The C-V and G-V measurements for the fabricated Pt gate MOS capacitor have been carried out in air, in a closed chamber upon exposure to various concentrations of H_2 (250 ppm to 2500 ppm) and NH_3 (25 ppm to 700 ppm) at various frequencies (15KHz, 25 KHz and 50 KHz) at room temperature (27 ^oC). The same characterizations have been carried out at various concentrations (50 ppm to 400 ppm) for CH_4 and (10 ppm to 100 ppm) for H_2S at 27 ^oC and 120 ^oC, respectively. The C-V and G-V measurements for CH_4 and H_2S are taken at 25 KHz. The fabricated MOS sensor has also been tested on above said gases by fully automated precision LCR meter HP-4284 A (frequency range 20 Hz to 1 MHz). The schematic of experimental setup used to study the C-V and G-V response of the fabricated device has been described in detail earlier in section 3.3.1, Chapter 3.

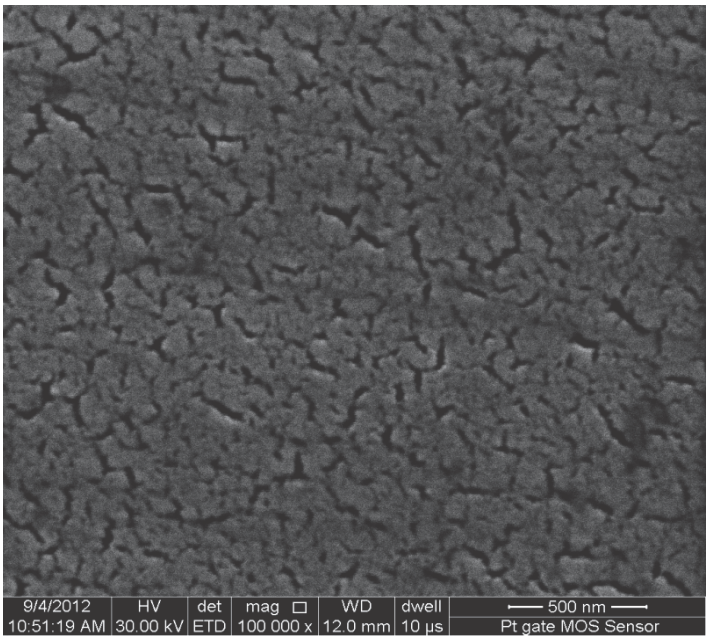

Fig.4.1 SEM image of Platinum (Pt) gate surface

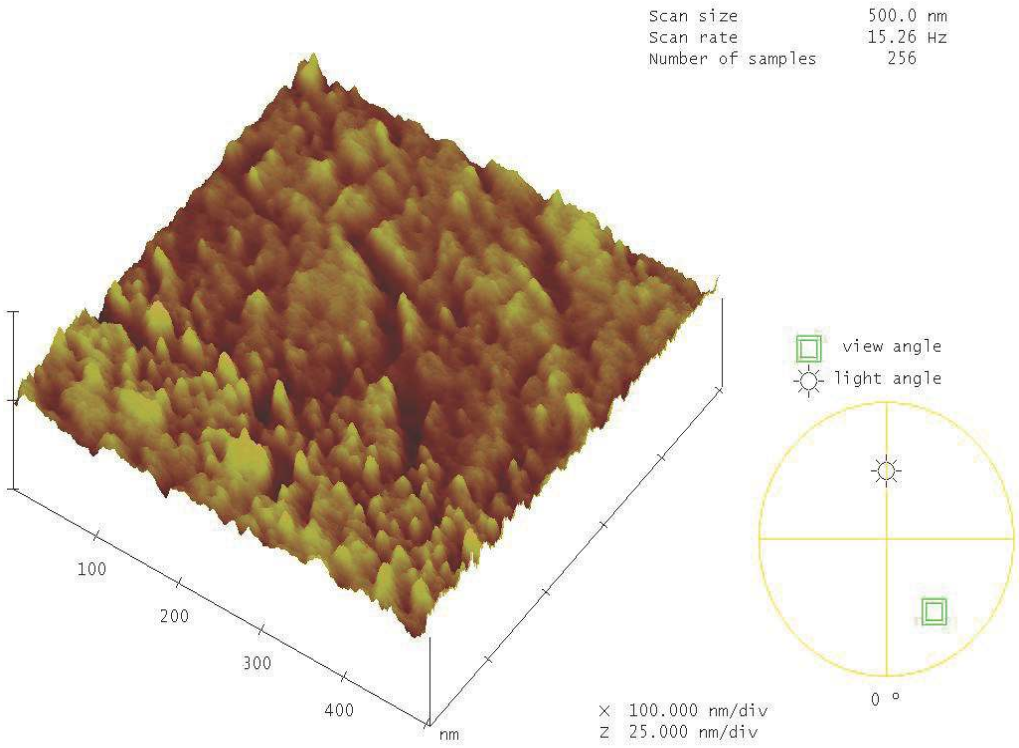

Fig.4.2 AFM image of Platinum (Pt) gate surface

4.3 Results

4.3.1 C-V and G-V Response for H_2, NH_3, CH_4, and H_2S

The gas sensing behavior of the fabricated gridded gate Pt/SiO_2/Si MOS sensor has been evaluated through C-V and G-V measurements in air, in a closed chamber upon exposure to different concentrations of H_2 and $NH_3$with various frequencies (15KHz, 25 KHz and 50 KHz) at room temperature (27 ^oC). The C-V and G-V characteristics for H_2 and NH_3 are illustrated in Fig. 4.3 to Fig.4.8 and Fig. 4.11 to Fig.4.16, respectively. The C-V and G-V response for CH_4 and H_2S at room temperature and 120 ^oC, respectively at 25 KHz are shown in Fig. 4.9 to Fig. 4.10 and Fig. 4.17 to Fig. 4.18, respectively. It is evident from the C-V characteristics (Fig. 4.3 to Fig. 4.10) as

the gas concentration increases capacitance of fabricated MOS sensor decreases at all the frequencies upon exposure to the test gases along with the shift in saturated capacitance value towards more negative side of the voltage axis [Yadava *et al*. (1990); Snow *et al*. (1965)]. The change in capacitance with gas concentration is converted into percentage sensitivity (S%) through the formula [Pandey *et al*.(2009(a))],

$$S\% = ((C_{air} - C_{gas})/C_{air})x100 = (\Delta C/C)x100 \quad (4.1)$$

Where, C_{air} and C_{gas} are the capacitances in air and gas, respectively.

In terms of capacitance, the maximum sensitivity of ~90% for H_2 was observed at 0.6 V gate bias voltage at 15 KHz (2500 ppm) as compared to other test gases at room temperature refer Fig. 4.19 to Fig. 4.26. The maximum sensitivity for NH_3, was found to be 85% (700 ppm) corresponding to gate bias 0.25 V at 15 KHz. The maximum sensitivity for CH_4 and H_2S was found to be 47 % (400 ppm) and 68% (100 ppm) corresponding to gate bias 0.15 V and -0.15 V, respectively at 25 KHz. Above results indicate that low frequency C-V response (15 KHz) of the device is better as compared to high frequencies (25 KHz and 50 KHz) for H_2 and NH_3. G-V characteristics (Fig. 4.11 to Fig. 4.18) of MOS capacitor shows the decrease in G value with concentrations for all test gases (H_2, NH_3, CH_4 & H_2S) along with shifting towards lower negative bias voltage for all above said frequencies and temperatures. It is evident from the (Fig. 4.11 to Fig. 4.18) that presence of test gases result in decrease of peak magnitude of the conductance. The percentage sensitivity (S%) in terms of change in conductance peak is defined as;

$$S(\%) = \frac{G_{p_i} - G_{p_{gas}}}{G_{p_i}} \quad (4.2)$$

Where, G_{p_i} = Conductance peak position in air and this is taken as reference.

$G_{p_{gas}}$ = Conductance peak position in presence of various test gases

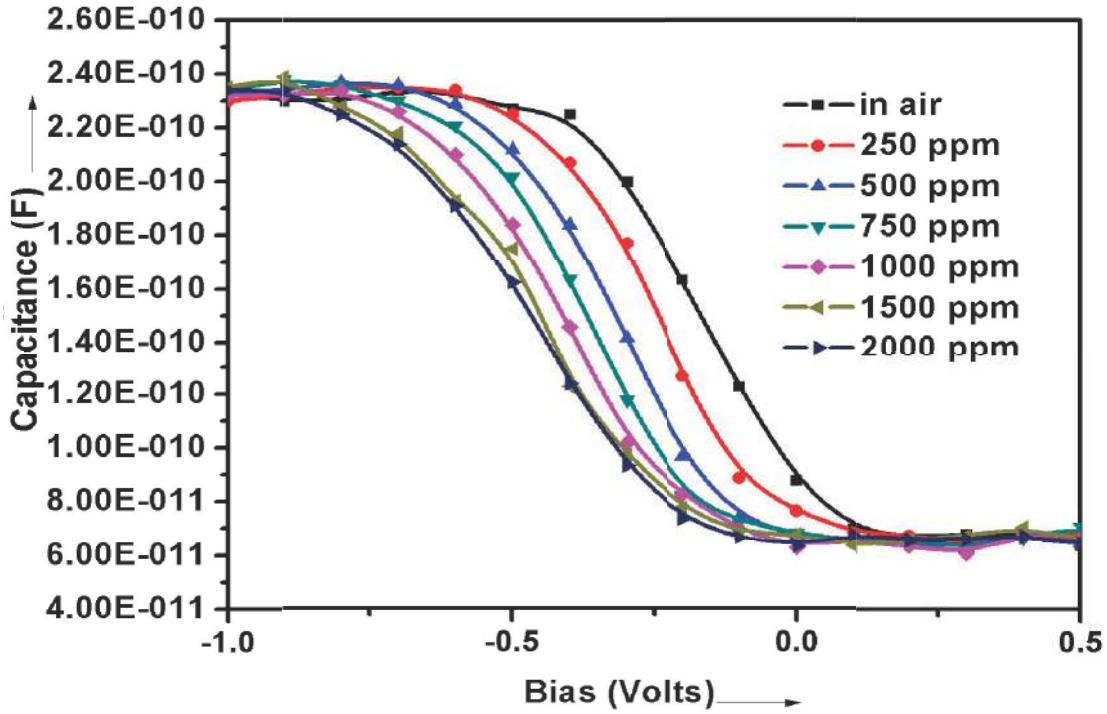

Fig. 4.3 C-V response of Pt gate MOS sensor for different concentrations of H_2 at f=15 KHz, room temperature

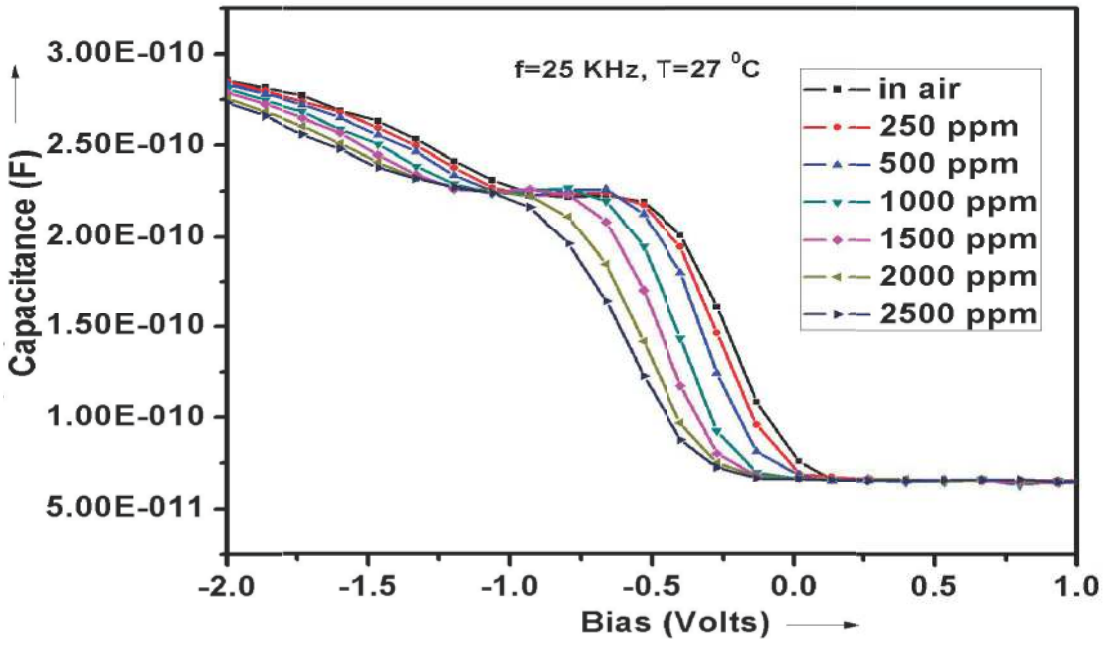

Fig. 4.4 C-V response of Pt gate MOS sensor for different concentrations of H_2 at f=25 KHz, room temperature

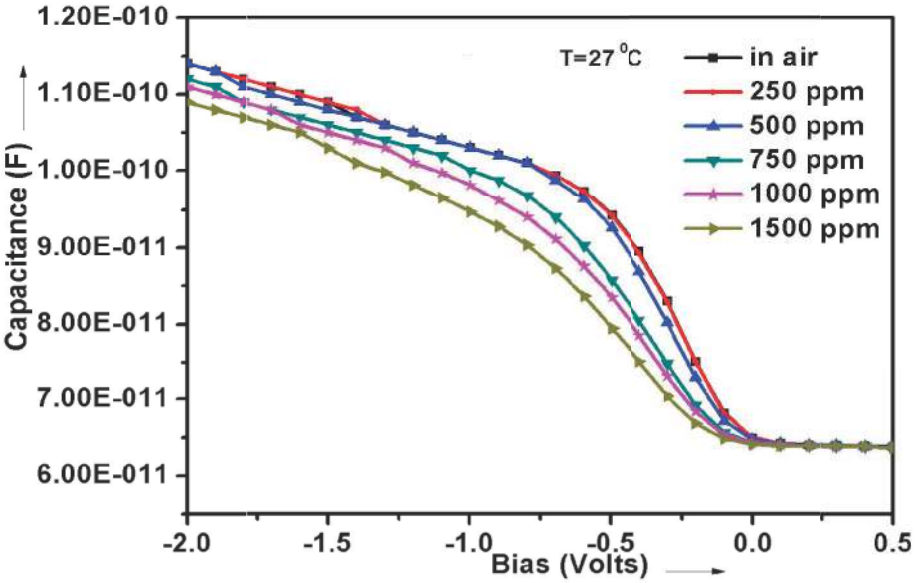

Fig. 4.5 C-V response of Pt gate MOS sensor for different concentrations of H_2 at f=50 KHz, room temperature

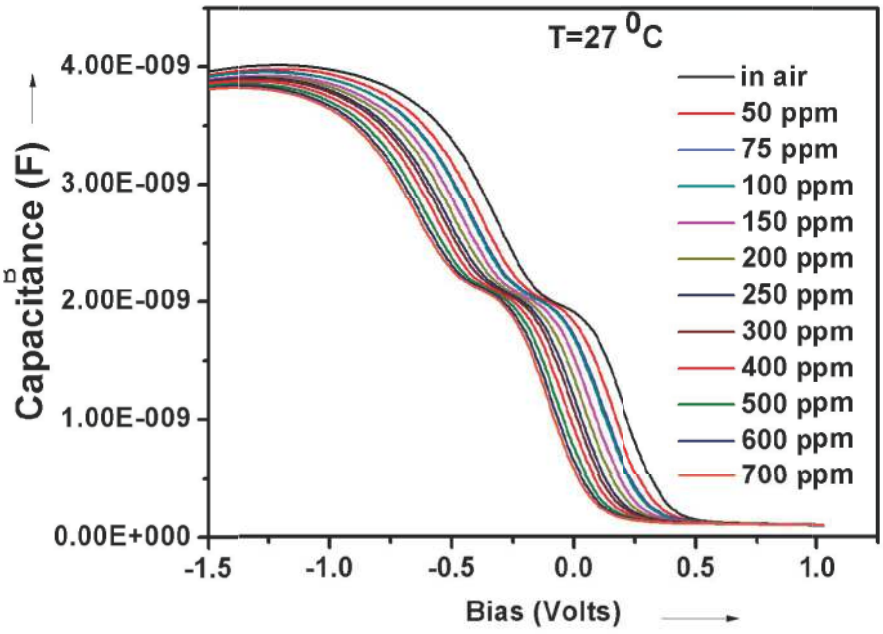

Fig. 4.6 C-V response of Pt gate MOS sensor for different concentrations of NH_3 at f=15 KHz, room temperature

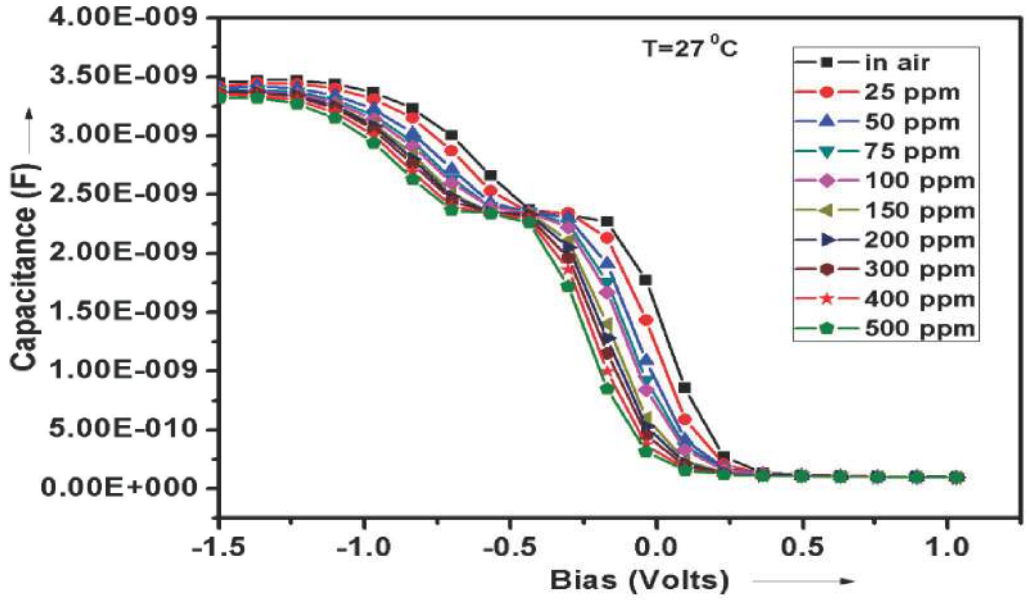

Fig. 4.7 C-V response of Pt gate MOS sensor for different concentrations of NH_3 at f=25 KHz, room temperature

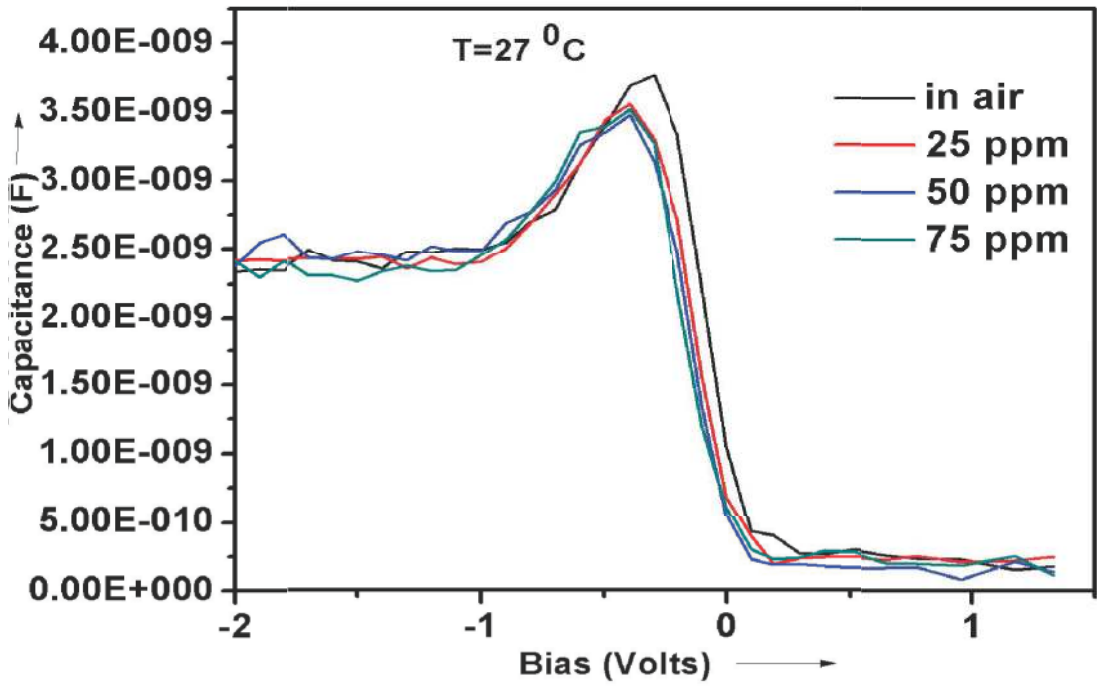

Fig. 4.8 C-V response of Pt gate MOS sensor for different concentrations of NH_3 at f=50 KHz, room temperature

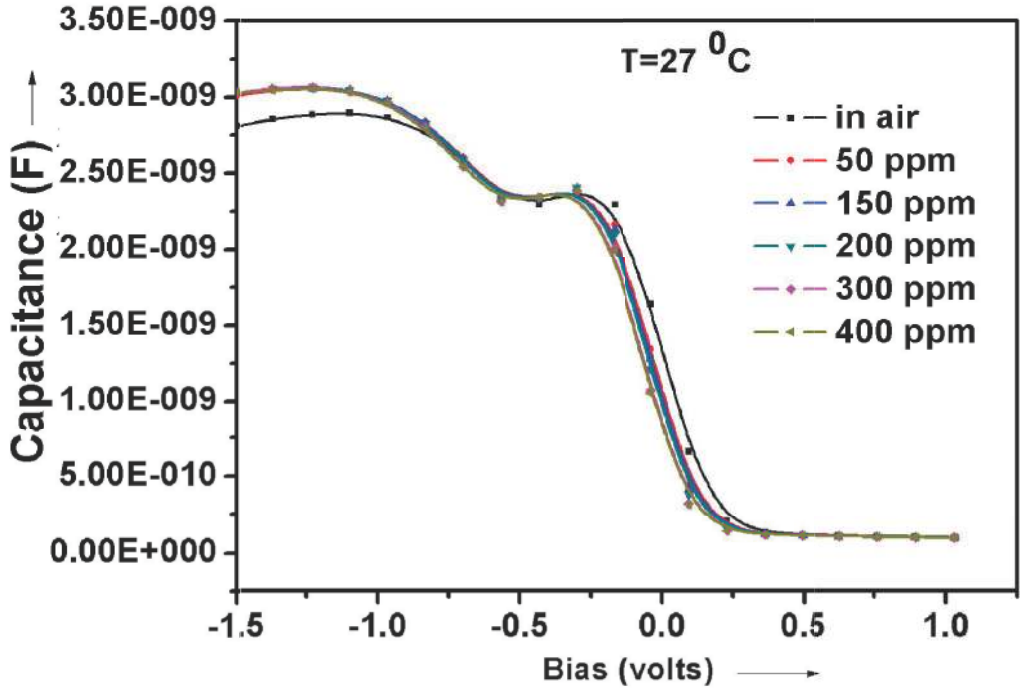

Fig. 4.9 C-V response of Pt gate MOS sensor for different concentrations of CH_4 at f=25 KHz, room temperature

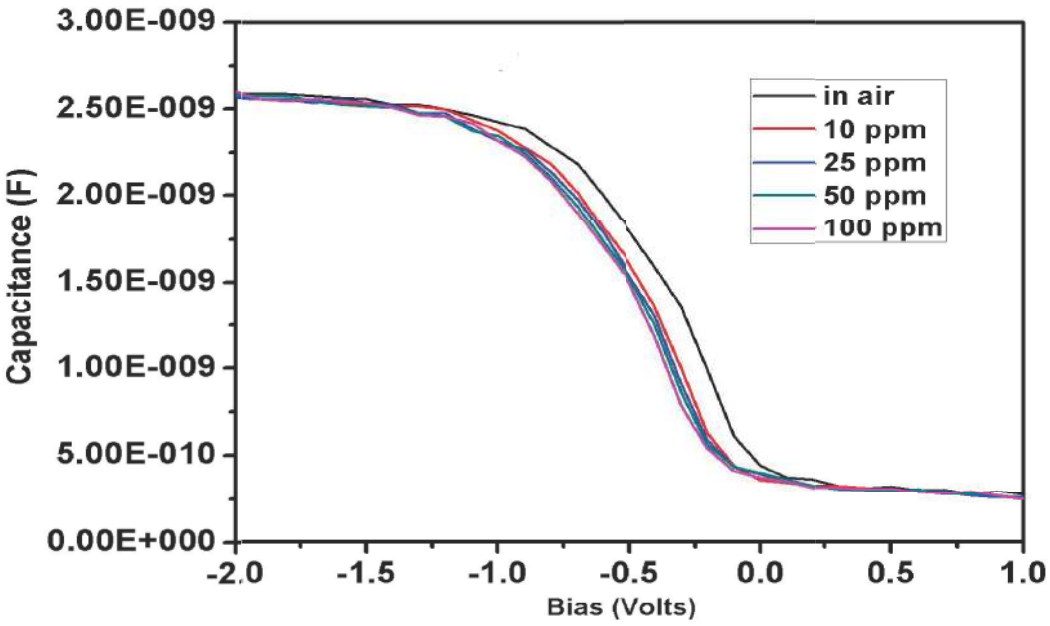

Fig.4.10 C-V response of Pt gate MOS sensor for different concentrations of H_2S at f=25 KHz, T=120 ^oC

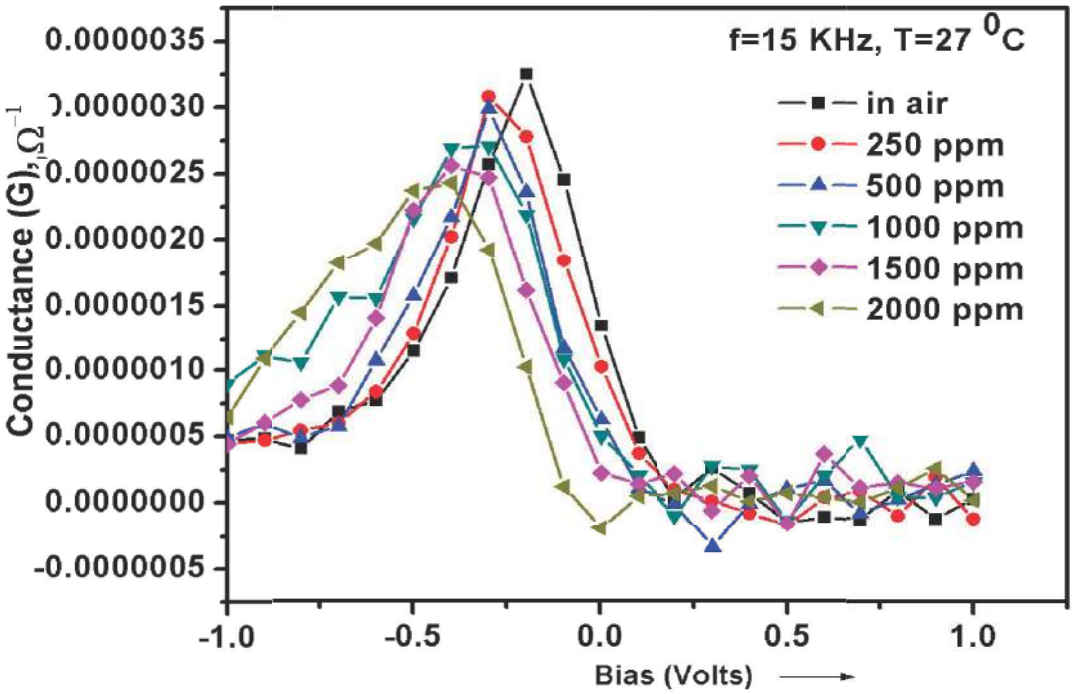

Fig.4.11 G-V response of Pt gate MOS sensor for different concentrations of H_2 at f=15 KHz, T=27 °C

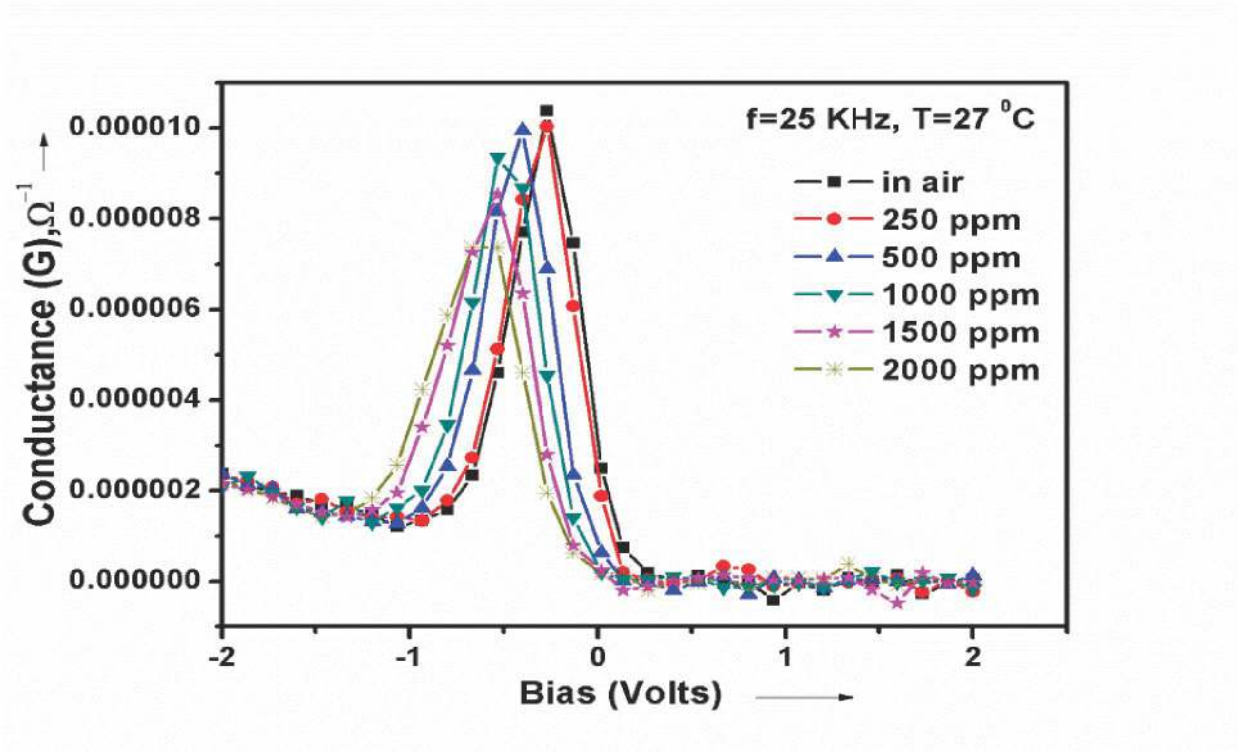

Fig.4.12 G-V response of Pt gate MOS sensor for different concentrations of H_2 at f=25 KHz, room temperature

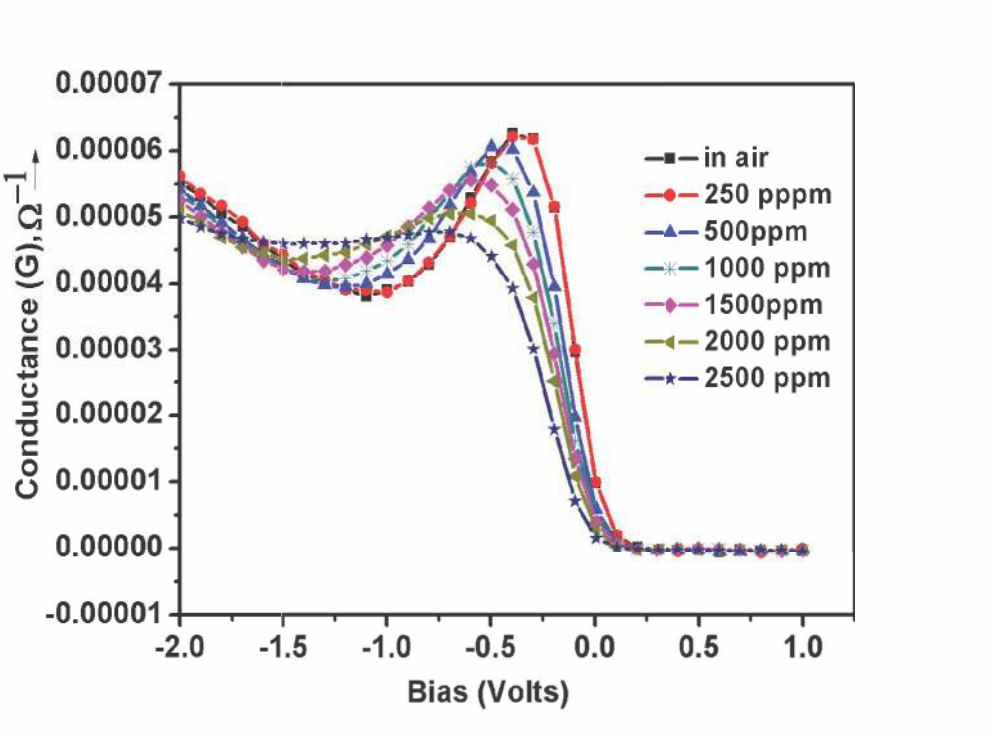

Fig.4.13 G-V response of Pt gate MOS sensor for different concentrations of H_2 at f=50 KHz, room temperature

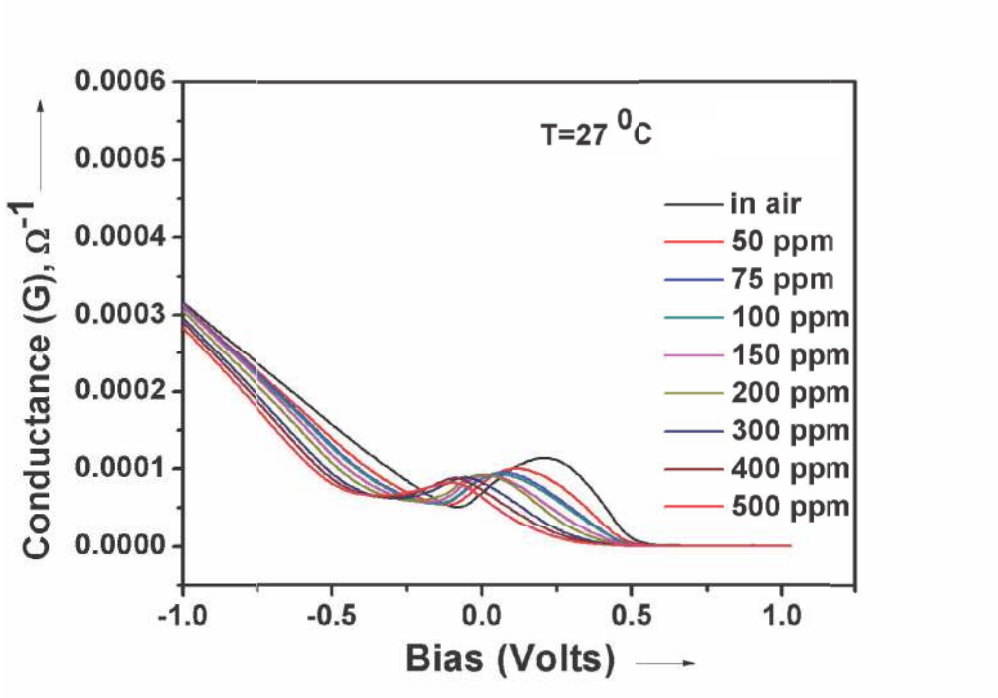

Fig.4.14 G-V response of Pt gate MOS sensor for different concentrations of NH_3 at f=15 KHz, room temperature

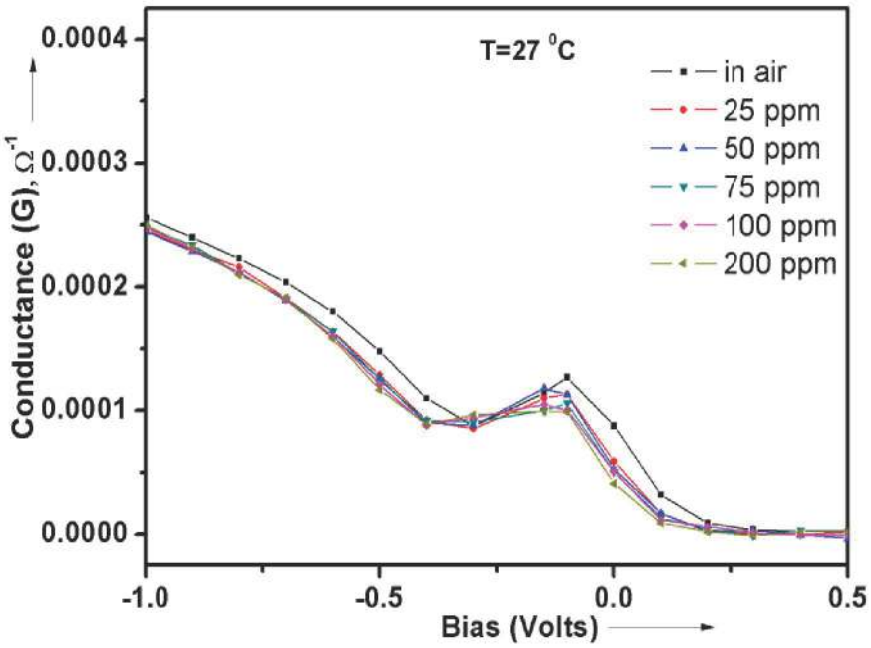

Fig.4.15 G-V response of Pt gate MOS sensor for different concentrations of NH_3 at f=25 KHz, room temperature

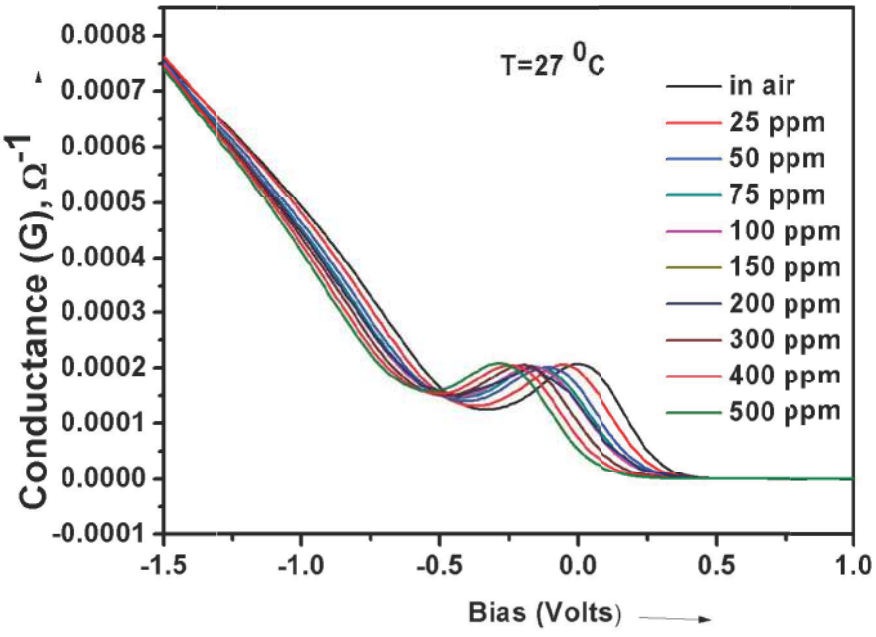

Fig.4.16 G-V response of Pt gate MOS sensor for different concentrations of NH_3 at f=50 KHz, room temperature

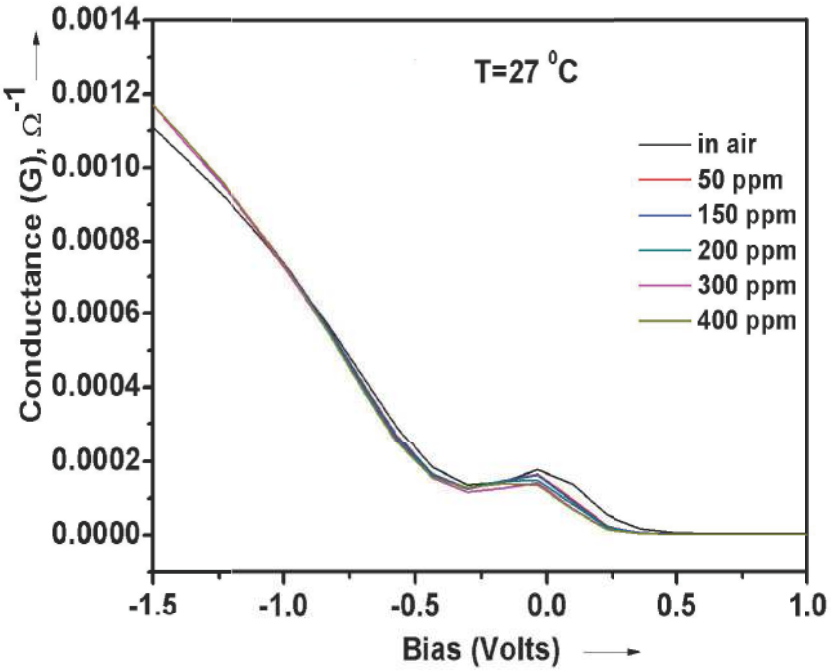

Fig.4.17 G-V response of Pt gate MOS sensor for different concentrations of CH_4 at f=25 KHz, room temperature

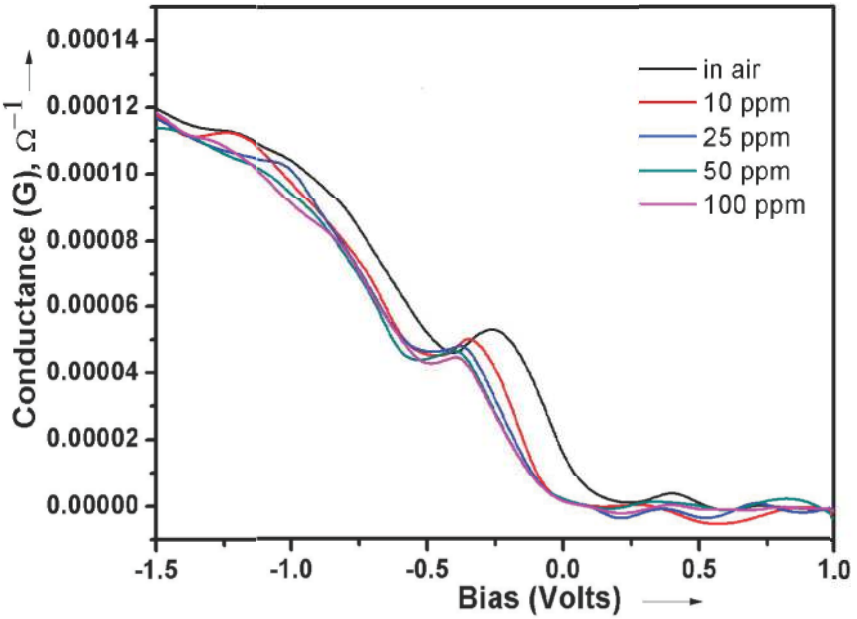

Fig.4.18 G-V response of Pt gate MOS sensor for different concentrations of H_2S at f=25 KHz, T=120 °C

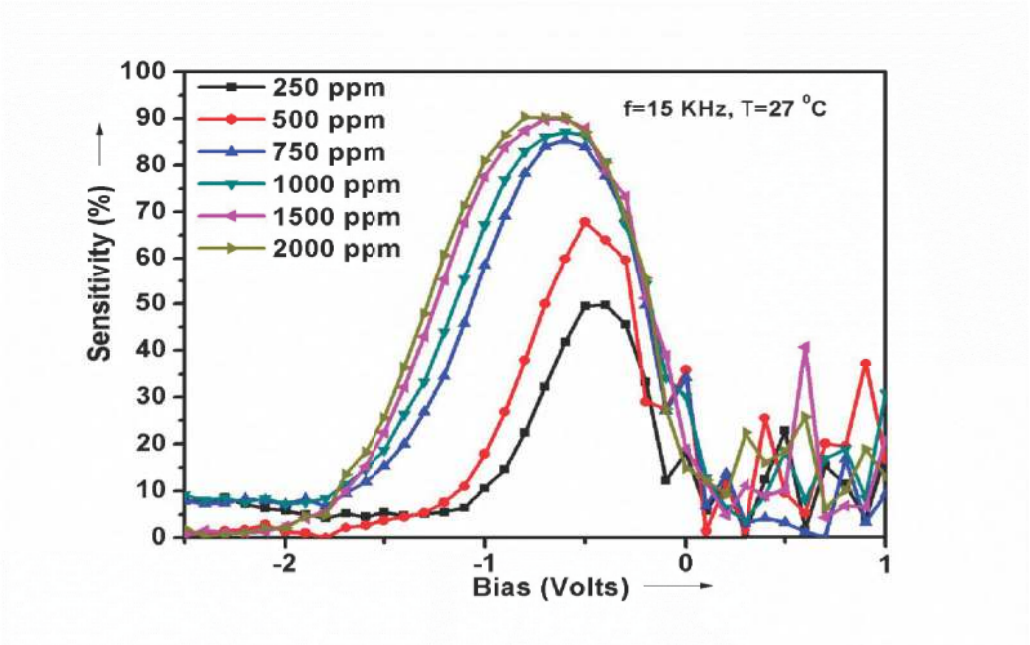

Fig.4.19 Sensitivity vs Bias voltage of Pt gate MOS sensor for different concentrations of H_2 at f=15 KHz, room temperature

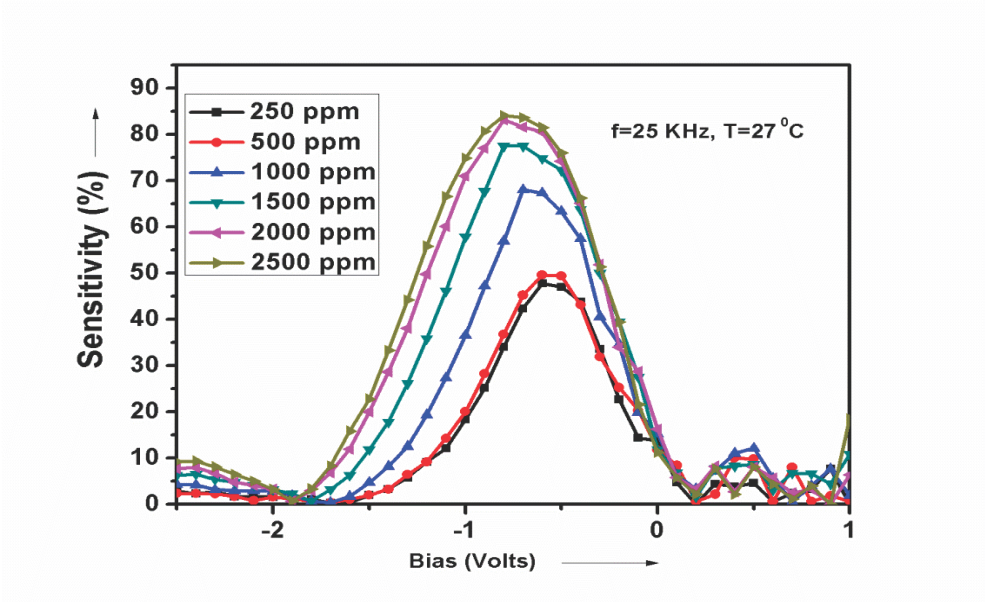

Fig.4.20 Sensitivity vs Bias voltage of Pt gate MOS sensor for different concentrations of H_2 at f=25 KHz, room temperature

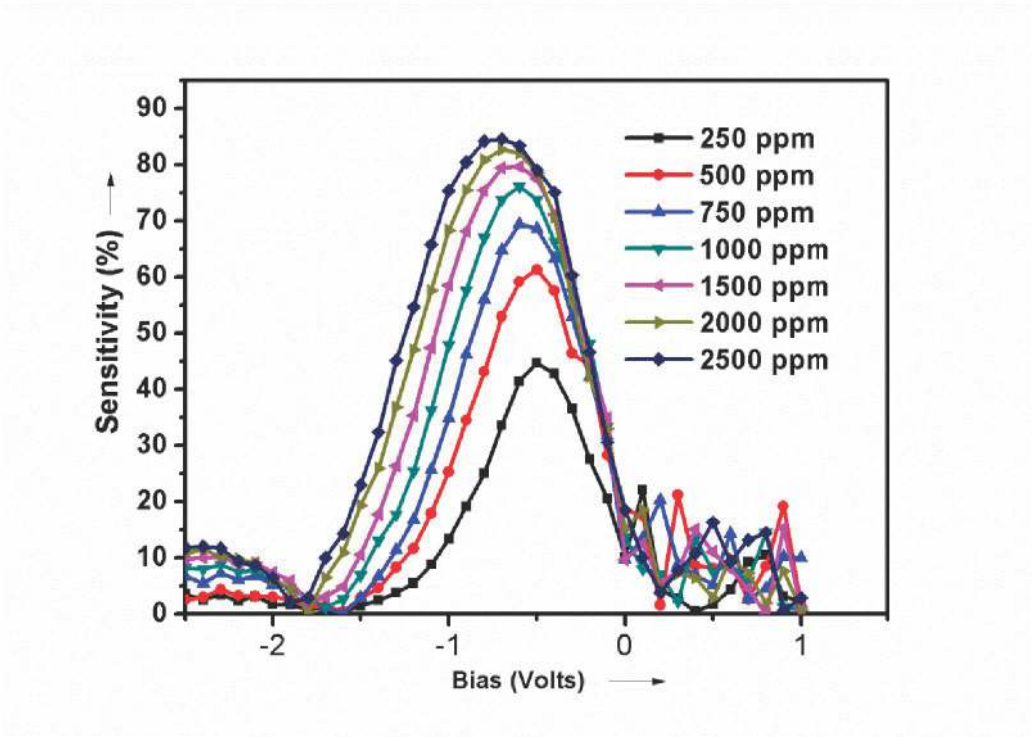

Fig.4.21 Sensitivity vs Bias voltage of Pt gate MOS sensor for different concentrations of H_2 at f=50 KHz, room temperature

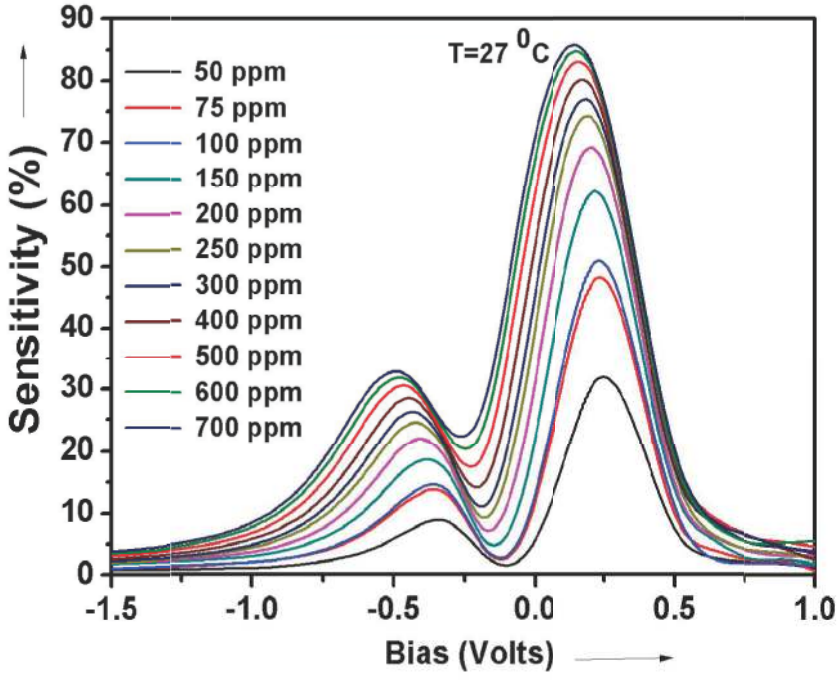

Fig.4.22 Sensitivity vs Bias voltage of Pt gate MOS sensor for different concentrations of NH_3 at f=15 KHz, room temperature

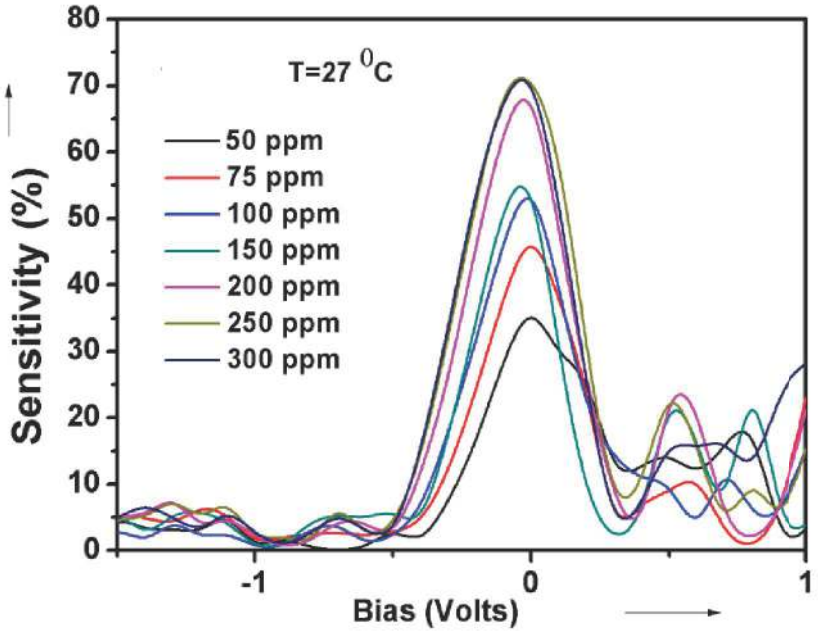

Fig.4.23 Sensitivity vs Bias voltage of Pt gate MOS sensor for different concentrations of NH_3 at f=25 KHz, room temperature

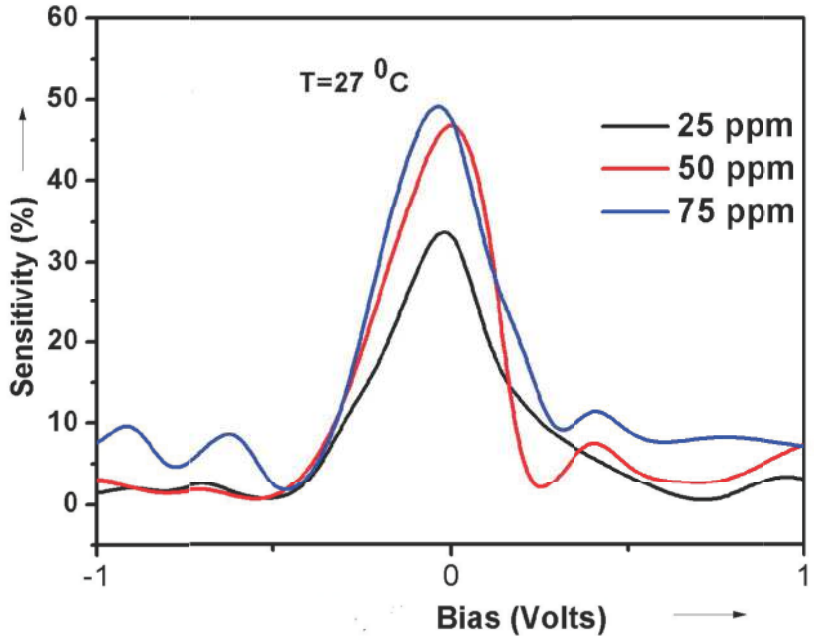

Fig.4.24 Sensitivity vs Bias voltage of Pt gate MOS sensor for different concentrations of NH_3 at f=50 KHz, room temperature

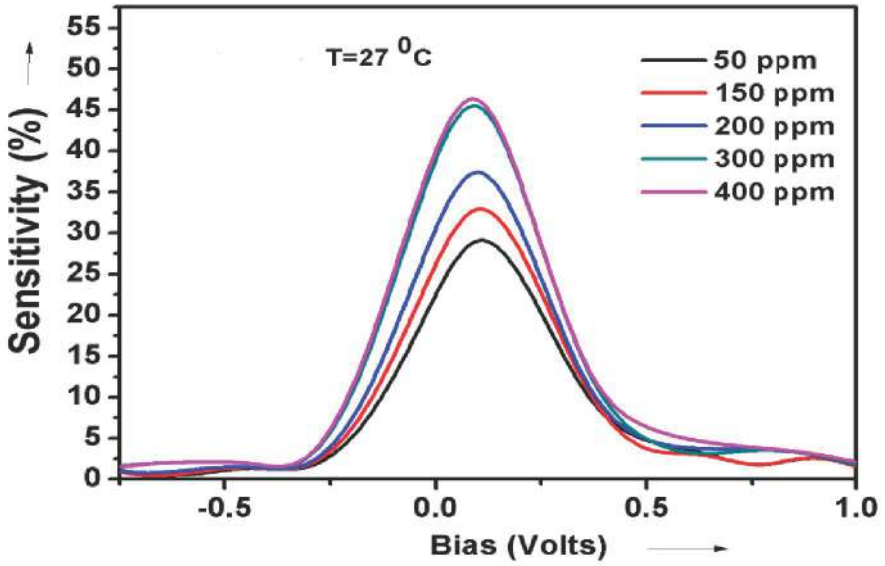

Fig.4.25 Sensitivity vs Bias voltage of Pt gate MOS sensor for different concentrations of CH_4 at f=25 KHz, room temperature

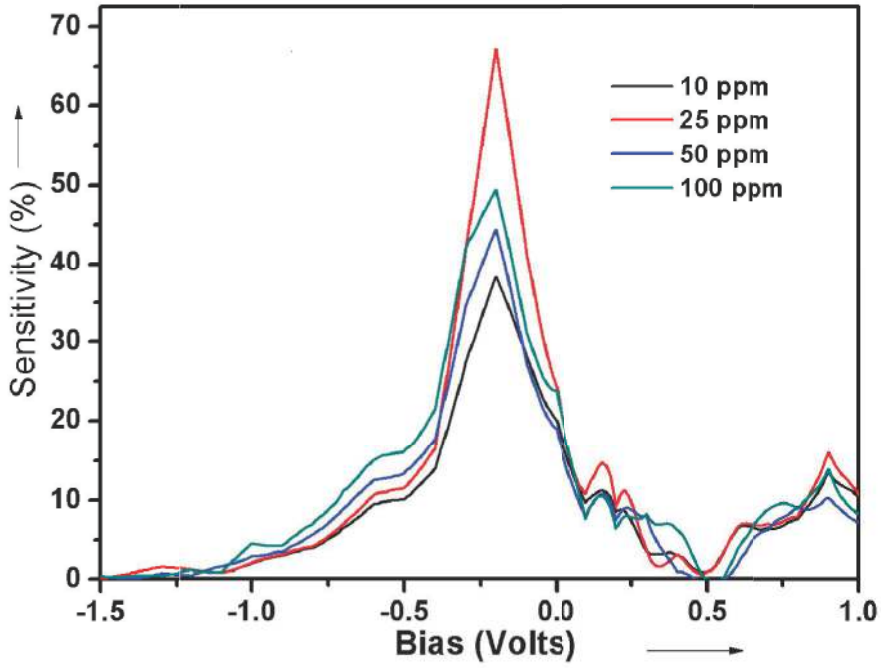

Fig.4.26 Sensitivity vs Bias voltage of Pt gate MOS sensor for different concentrations of H_2S at f=25 KHz, 120 ^oC temperature

The shift in conductance peak position decreases with increase in frequency and gas concentration. The change in conductance peak was found to be maximum at lower frequency. The maximum change in conductance peak position was found to be 45.66%, 27.88% for H_2 and NH_3 respectively, at 15 KHz. The change in conductance peak was observed 23.4%, 14.7% for CH_4 and H_2S**,** respectively at 25 KHz. Gridded gate Pt/SiO_2/Si MOS sensor shows a good capability to detect a low concentration 25 ppm, 50 ppm, 10ppm of NH_3, CH_4 and H_2S, respectively.

It has been further observed that the capacitance as well as conductance value and their peak position change with signal frequency and gas concentration yielding better results at lower frequencies.

4.3.2 Evaluation of Interface Trap Charge Density (N_{it}) by Low Frequency Conductance Method

The interface trap density N_{it} has been evaluated for test gases from the G-V curves and results are shown in Fig. 4.27 to Fig. 4.30. The trap charges for H_2 and NH_3 are evaluated at various frequencies (15 KHz, 25 KHz and 50 KHz) and for CH_4 and H_2S at 25 KHz at different concentrations. The interface trap charge density (N_{it}) has been evaluated for (H_2, NH_3, CH_4) at room temperature and for H_2S at 120 ^oC, in air. The interface trap level density N_{it} is calculated from peak value of G-V curve. For uniform distribution of interface trap level over the Si band gap, the G_p/ω versus $\omega\tau_p$ curve has one peak at $\omega\tau_p$=1.98. The interface trap density (N_{it}) is evaluated by the following formula [Altindal *et al.* (2005)].

$$N_{it} = \frac{\left[\frac{G}{\omega}\right]_{\max}}{0.40q} \tag{4.3}$$

Where,

ω- Applied angular frequency

τ_p - Interface capture time.

and $\omega\tau$=1.98

Fig. 4.27 to Fig. 4.30 show that the interface trap density decreases as the gas concentration increases. Variation of interface trap charges with various frequencies for H_2 and NH_3 is shown in Fig. 4.27 and Fig. 4.28, respectively. The interface trap charge density (N_{it}) was found to be maximum at lower frequency (15 KHz) for H_2 and NH_3 both.. The variations of N_{it} with gas concentration for other test gases (CH_4 and H_2S) at 25 KHz are shown in Fig. 4.29 to Fig.4.30, respectively. It is clear from Fig. 4.27 and Fig. 4.28 that N_{it} decreases with increasing measurement frequency and gas concentration.

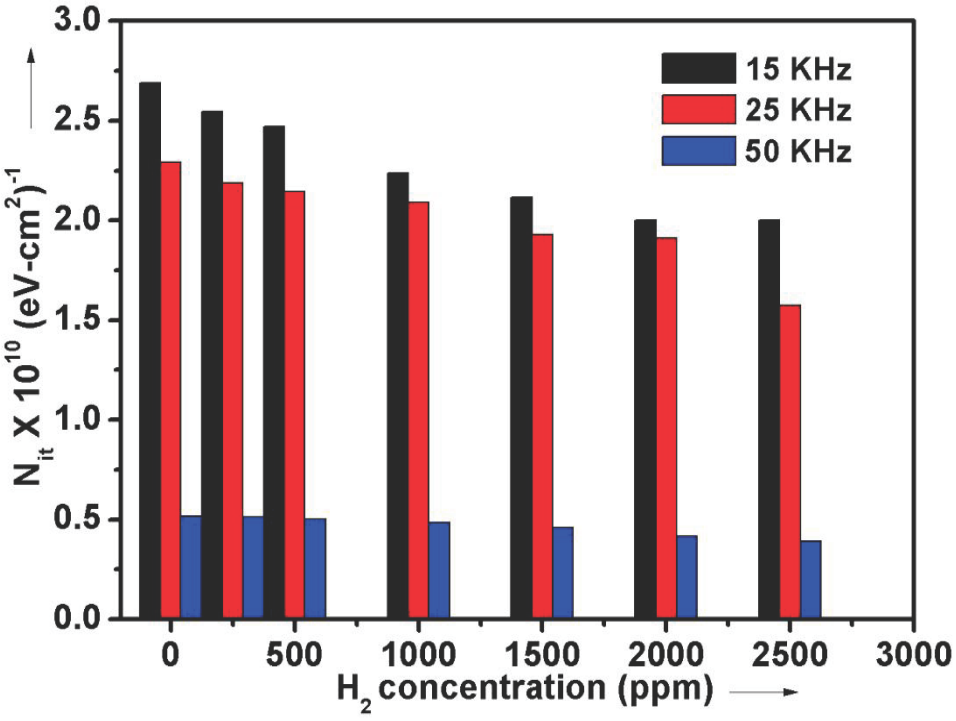

Fig. 4.27 Interface Trap charge (N_{it}) vs Concentraion of Pt gate MOS sensor for different concentrations of H_2 at f=15KHz, 25 KHz and 50 KHz, room temperature

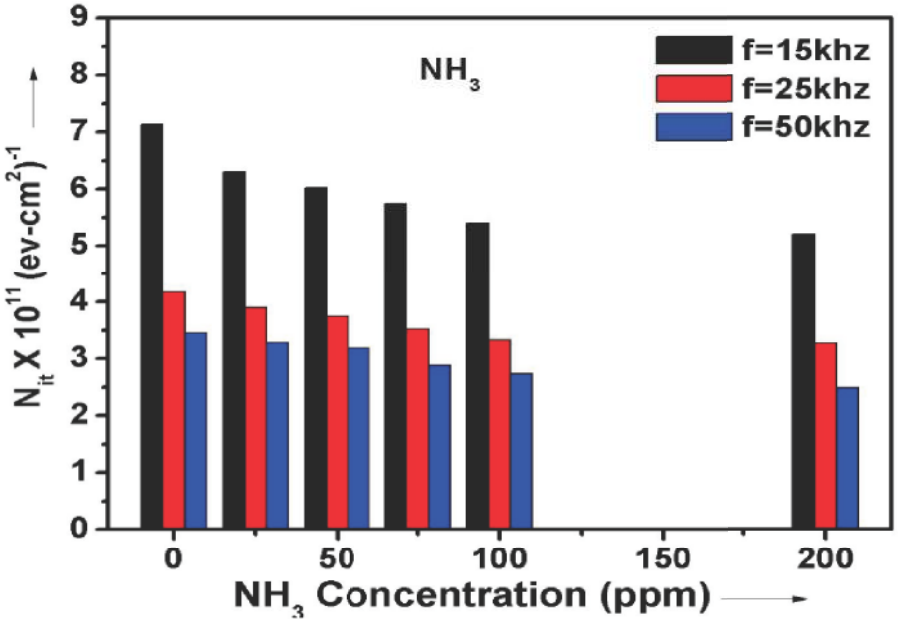

Fig.4.28 Interface Trap charge (N_{it}) vs Concentraion of Pt gate MOS sensor different concentrations of NH_3 at f=15 KHz, 25 KHz and 50 KHz, room temperature

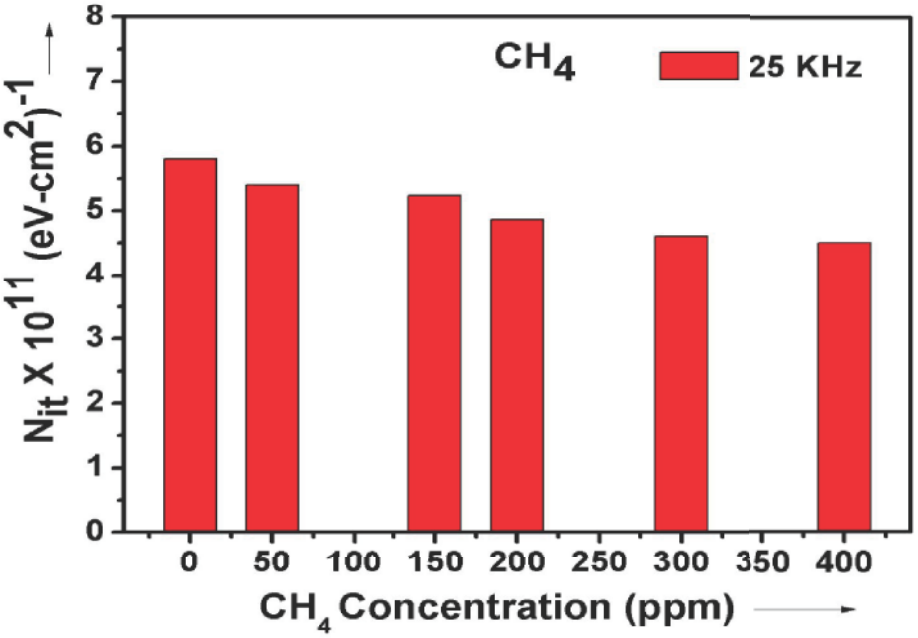

Fig. 4.29 Interface Trap charge (N_{it}) vs Concentraion of Pt gate MOS sensor for different concentrations of CH_4 at f=25KHz, room temperature

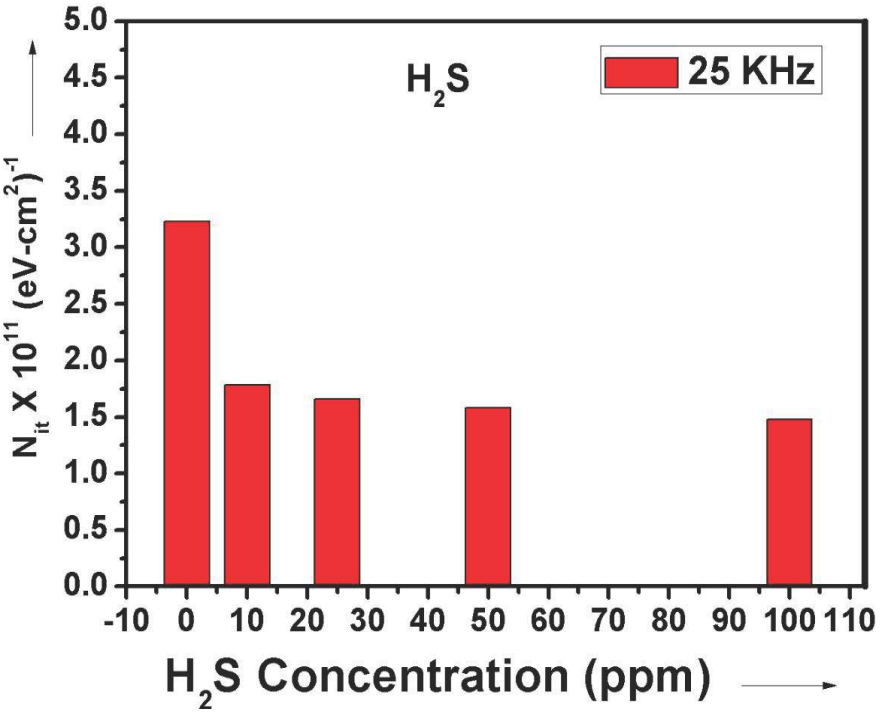

Fig. 4.30 Interface Trap charge (N_{it}) vs Concentraion of Pt gate MOS sensor for different concentrations of H_2S at f=25KHz, 120 ^oC temperature

4.4 Discussion

Gas sensing behavior of such MOS sensors for H_2 in air, several sensing mechanisms had been reported by several researchers [Snow *et al.* (1965); Shivaraman *et al*. (1976); Lundstrom *et al*. (1981) and Lundstrom *et al*. (1995)]. They had reported that the catalytic gate MOS sensor adsorbed H_2 molecules upon exposure to H_2 gas. These H_2 molecules are then dissociated into atomic form and diffused through the porous transition metal gate electrode to the metal-insulator interface. At the interface these H_2 atoms form a dipole layer which decreases the effective work function of transition metal which results in the decrease in flat band voltage of the MOS capacitor [Lundstrom (1981); Shivaraman *et al*. (1976)] and causes a parallel shift in C-V characteristics towards -ve voltage axis [Snow *et al*. (1965); Sze (1981); Soo *et al*. (2010)]. Hydrogen sensing mechanism of conventional Pt/SiO_2/Si is shown in Fig. 4.31(c).The increase or decrease in the value of G-V curve under the influence of H_2 depends mainly on the nature of interface traps.

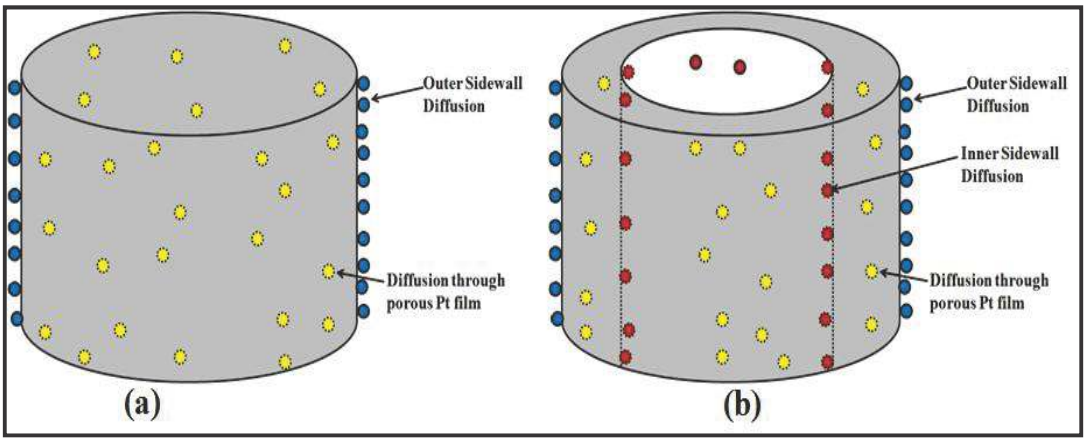

Fig. 4.31 Illustration of sensing mechanism of (a) ungridded and (b) gridded gate structure

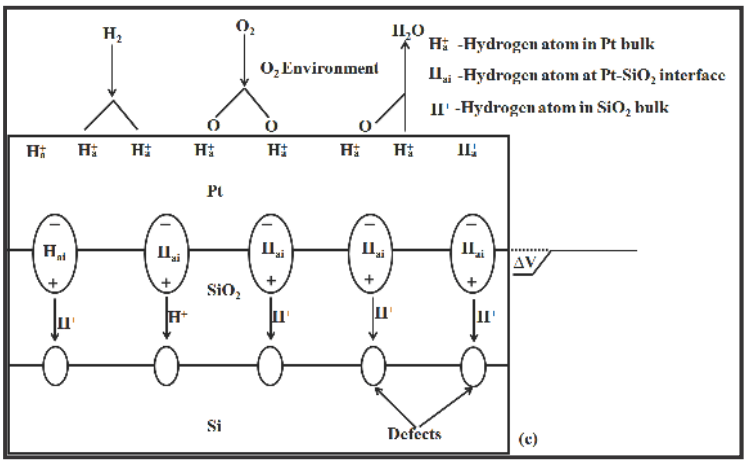

Fig. 4.31(c) Illustration of H_2 detection principal of conventional Pt/SiO_2/Si MOS sensor

Vavilov *et al*. [Vavilov *et al.* (1990)] reported that surface state density decreases as H_2 atoms interact with dangling bonds in Silicon. Hence, peak conductance value of G-V curve decreases with increasing concentration of H_2.

An interface trap is considered to be donor if it can become neutral or positive by donating an electron. An acceptor interface trap can become neutral or negative by accepting an electron [Sze (1987)]. For thick gate Pd MOS device, with a thin gate oxide, it has been observed that interface state density increases in some regions and decreases in other regions of the band gap [Evans *et al*. (1986); Fare and Zemel (1987)] with H_2 exposure. This can be explained by assuming that some H_2 atoms reach the SiO_2/Si interface via diffusion to the SiO_2 film. The majority of these atoms

are trapped by various defects which are available at the SiO_2/Si interface. Some atoms participate in the formation of neutral complexes with acceptor surface state, while other atoms supply electrons to conduction band those are attached at this interface as protons [Gaman *et al*. (1999)].

In the present study, similar gate with slight modification viz. gridded structure of Platinum (Pt) has been used instead of a palladium (Pd) layer. Thus, the gas sensing mechanism follows the same steps as in case of Pd gate but with improved diffusion and dissociation of gas molecules due to gridded structure [Shivaraman *et al*. (1976); Lundstrom *et al*. (1981)]. The porous structure of the Pt films may be the reason of enhanced sensitivity of the fabricated MOS structure. The porosity in the Pt film was confirmed through SEM and AFM studies as shown in Fig. 4.1 and Fig. 4.2.

Apart from the above discussed gas sensing mechanism in MOS sensor, the reaction of reducing gases like H_2, NH_3, CH_4 and H_2S with Oxygen is another reason for high sensitivity. The atmospheric oxygen on the surface of metal gate can dissociate into oxygen atoms which may move through the porous surface to the Pt/SiO_2 interface and get polarized. These polarized negatively charged ions can penetrate through thin oxide layer and reach the SiO_2/Si interface. On exposure to the reducing gases (H_2, NH_3, CH_4 and H_2S), they interact with oxygen atoms on the interfaces and decrease the concentration of negatively charged ions. This leads to decrease in surface state density and consequently the shift in C-V characteristics, which ultimately causes the increase in sensitivity [Ryzhikov *et al*. (2010)]. Fig. 4.31(a) and Fig. 4.31(b) show the H_2 diffusion mechanism (side wall diffusion) in ungridded and gridded Pt gate structures, respectively. Fig.4.31(c) illustrates the reaction mechanism of the conventional Pt/SiO_2/Si MOS sensor for H_2 in air. Trinchi *et al*. [Trinchi *et al*. (2008)] reported the spillover mechanism of H_2 onto oxide layer. According to this mechanism, H_2 molecules dissociate into atomic H_2 on the Pt metal film. After that they move onto the areas of the oxide layer which is not covered by the metal, where they become adsorbed. Thus O_2 ions which are present in the ambient are adsorbed on the oxide layer surface. They can react with the spill-over H_2 ions producing water and an electron, which increases electrical conductivity of the layer.

In the case of ammonia-sensitive devices, the sensing mechanism is not completely understood. It has earlier been suggested that it is due to hydrogen dipoles created by the decomposition of ammonia, as in the case of the hydrogen sensor [Winquist *et al.*

(1983)]. This results in decrease in work function of gate metal film. Several theories had been postulated to explain how the change in work function occurs. It has been suggested that a chemisorbed hydrogen containing gas undergoes catalytic dissociation on the transition metal electrode to yield atomic hydrogen, which is then absorbed into the gate metal causing a direct change in the metal work function [Ruths et al. (1981) ; Lewis (1967)], which results in the decrease in flat band voltage of the MOS sensor and causes a parallel shift in C-V characteristics towards -ve voltage axis [Snow *et al.* (1965); Sze S.M.(1981); Soo *et al*. (2010)]. However, that there is a qualitative difference in the detection mechanisms for hydrogen and ammonia. It has been suggested by several researchers [Lundstrom *et al*. (1986(a&b))] that the surface potential change of the metal caused by these dipoles is capacitively coupled to the semiconductor surface through the oxide and the stray capacitance between the metal and the oxide. The capacitively coupled model for ammonia sensitivity is shown in Fig. 4.32. It is suggested that change in surface potential of any porous conducting layer can be used to change the field at a semiconductor surface and hence for detection of any gaseous species that causes this potential change, which is responsible for the detection of a gaseous species [Lundstrom *et al*. (1986(a&b))**].**

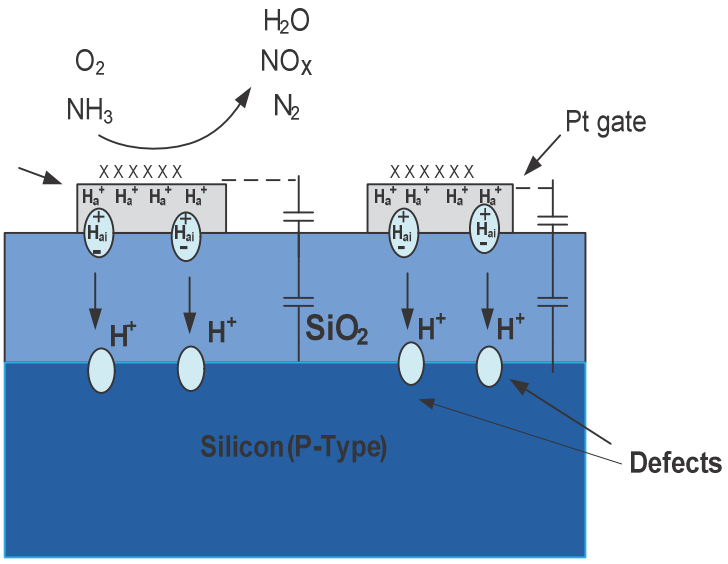

Fig. 4.32 Capacitively coupled model for thin porous catalytic metal film surface for NH_3 sensing

The chemical reaction of ammonia in presence of air onto the surface of Pt/SiO_2/Si MOS sensor can be represented by as follows

$NH_{3(gas)} \rightleftharpoons NH_{3(ads)}$

$NH_{3\,(ads)} \rightleftharpoons xH\ (ads) + NH_{(3-x)\,(ads)}$

$2H_{(ads)} \rightleftharpoons H_{2\,(ads)}$

$H_{2\,(ads)} \rightleftharpoons H_2\ (gas)$

$2H_{\,(ads)} + O_{(ads)} \longrightarrow H_2O_{\,(ads)}$

$H_2O_{\,(ads)} \longrightarrow H_2O_{\,(gas)}$

$NH_{(3-x)}\ (ads) + O\ (ads) \longrightarrow$ Further oxidation product

Where, $x \leq 3$.

and ads - adsorption

The reaction of methane with Pt/SiO_2/Si MOS sensor has already been proposed [Kim *et al.* (2001)].

$CH_4 + O_2 \xrightarrow{Pt} CO_2 + 2H_2$

Now the dissociated H_2 will further react with O_2 ions which are available on SiO_2

[Lundstrom *et al*. (1977); Mishra and Agarwal (1994)].

$H_{2(gas)} + O^-_{ads}(SiO_2) \longrightarrow H_2O_{(gas)} + (SiO_2) + e^-$,

$H_{2(gas)} + O^{2-}_{ads}\,(SiO_2) \longrightarrow H_{2(gas)} + 2e$-

Or

$H_{2(gas)} + O_{ads}(Pt) \longrightarrow H_2O$,

Where, $O_{ads}(Pt)$ - oxygen adsorb at Platinum (Pt), $O^-_{ads}(SiO_2)$ - oxygen ion adsorb at SiO_2.

If O(Pt) is more reactive than $O^{2-}(SiO_2)$.

In addition to this, molecular hydrogen (H_2) gets dissociated into atomic form (H) at Pt surface resulting into the following chemical reactions

$H_{2(gas)} \longrightarrow H + H$, $\quad H + SiO_2 \longrightarrow H_{ads}\,(SiO_2)$,

$H_{ads}(SiO_2) + O^-_{ads}(SiO_2) \longrightarrow OH^-_{ads}(SiO_2)$

$OH^-_{ads}(SiO_2) + H_{ads}(SiO_2) \longrightarrow H_2O(g) + (SiO_2) + e^-$

It has also been found that gridded Pt/SiO_2/Si MOS transistor is sensitive to H_2S at 120 ^oC. It is possible due to the catalytic dissociation of H_2S at 120 ^oC. Even though this sensor does not respond at room temperature this is due to the lower activation energies for H_2S dissociation and adsorption at the room temperature [Weixin and Yibing (1988)]. The gridded gate MOS sensor works in the following way. First H_2S molecules are dissociated into hydrogen and sulphur atoms, which are adsorbed on the Pt surface. The resulting hydrogen atoms partly penetrate the Pt metal film to the Pt/SiO_2 interface and give rise to a dipole layer [Ruths *et al*. (1981)]. The dipole layer alters the work function difference between the metal and the semiconductor, thereby changing the threshold voltage of the MOS sensor [Lundstrom *et al*. (1986(a)), Lundstrom and Distefano (1976)]. It is observed that the H_2S sensitivity of Pt/SiO_2/Si MOS sensor was found to be increase with increase in temperature. The variation of temperature appears not to influence the H_2S sensing mechanism of the device. We suppose that the increase of sensitivity with temperature is due to an increase of the rate constant for H_2S dissociation and adsorption on a Pt surface [Weixin and Yibing (1988)]. It has been illustrated in Fig. 4.33 that in the presence of O_2, water molecules are formed on the Pt surface, which influences the number of H_2 atoms available at the Pt-SiO_2 interface [Lundstrom *et al*. (1986(a))]. Besides this, the reaction of sulphur and O_2 takes place on the Pt gate, i.e., the regeneration process can be attributed to a formation of SO_2. It has also been observed that Pt gate is inactivated by adsorbed sulphur atoms. These sulphur atoms occupy some of the activation sites directly affecting the porosity of the metal gate which intern prevent some H_2 atoms to reach at Pt-SiO_2 interface. Occupied activation sites also prevent O_2 to reach at the interface resulting in poor recovery of Pt gate MOS sensor. The performance of the H_2S can be restored by thermal treatment of ~ 30 minutes at a temperature more than 200 ^oC and good ventilation in air [Weixin and Yibing (1988)]. The additional shift in C-V response is due to (H+) ions entering into the insulator (SiO_2) layer [Lundstrom *et al*. (1986), Nylander *et al*. (1984)].The reaction mechanism of of Pt gate MOS sensor is proposed as follows [Truex *et al*. (1999)].

$$H_2S + 1.5\ O_2 \longrightarrow (SO_2)_{gas} + H_2O \qquad (4.4)$$

$$(SO_2)_{gas} \longleftrightarrow (SO_2)_{ads} \quad (4.5)$$

$$(SO_2)_{ads} \longleftrightarrow (SO)_{ads} + (O)_{ads} \quad (4.6)$$

$$(SO)_{ads} \longleftrightarrow (S)_{ads} + (O)_{ads} \quad (4.7)$$

It is seen from the above reaction steps that SO_2 is adsorbed on Pt metal gate in the form of $(S)_{ads}$ and $(O)_{ads}$. Equations (4.5) and (4.6) have very fast kinetics with high sticking coefficients for SO_2 adsorption. Reaction (4.7) is relatively slower and its kinetics can be increased by exposure to reducing gases like as H_2, CO etc. which removes $(O)_{ads}$ from the surface but do not remove the more strongly bound $(S)_{ads}$ due to its high sticking coefficient. Conversely, oxygenated surfaces or exposure to O_2 inhibit dissociative adsorption and reduce the formation of $(S)_{ads}$ on the Pt metal gate surface. The formation of these strongly adsorbed sulphur species on the catalyst surface can effectively block the adsorption of reaction molecules which results reduction in overall catalyst activity of the gate.

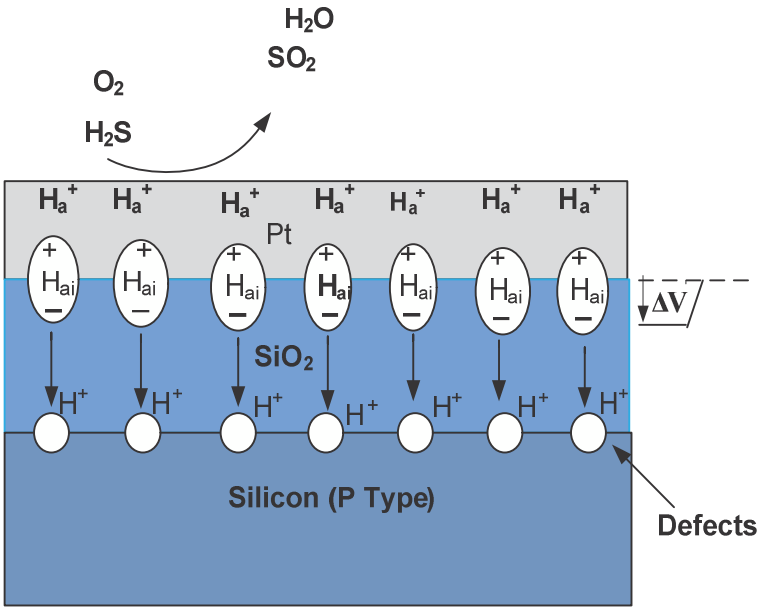

Fig. 4.33 Reaction mechanism of Pt/SiO_2/Si MOS sensor for H_2S

Another possible mechanism for detection of H_2 and other H_2 containing gases in gridded Pt/SiO_2/Si MOS sensor for improved sensitivity appears to be primarily due to side diffusion of these molecules because of gridded structure of the sensor as shown in Fig. 4.31(b). Such side diffusion has been reported earlier for the detection of Carbon Monoxide (CO) using Pd MOS sensor [Dobos *et al.* (1980); Soderberg and

Lundstrom (1980)]. It is obvious from Fig. 4.31(c) to Fig. 4.33 that internal sensing mechanism of all MOS sensors remains same for all H_2 containing gases. On the basis of above discussed mechanism for sensitivity, the enhanced sensitivity of the MOS capacitor based devices in the present study can be attributed to the following reasons: (i) the porous and gridded gate structure increases the diffusibility of H_2 so that more number of H_2 atoms will reach at Pt-SiO_2 interface which forms the strong dipole layer at the interface results in decrease in Pt work function causes decrease in the flat band voltage and linear increase in fixed surface state density [Johnson *et al*. (1975); Yamamoto *et al*. (1980); Yadava *et al*. (1990)], (ii) side wall diffusion also plays dominant role to increase the sensitivity of the fabricated device. Due to inner side wall effective surface area of the gridded structure increases as compared to ungridded structure [Dobos *et al*. (1980); Soderberg and Lundstrom (1980); Tan *et al.* (2008)]. So that more H_2 molecules dissociate into atomic form and these H_2 atoms enter into oxide layer which results in decrease in interface state density causes increase in sensitivity [Pandey *et al*. (2009(b)], (iii) spillover of H_2 atoms through oxide layer [Lundstrom *et al.* (1981)], (iv) better chemical absorption of H_2 in air ambient atmosphere in gridded Pt/SiO_2/Si MOS sensor. In air, ambient anions (like O_2^-, O^-, and O^{2-}) on Pt surface will be more. The chemical bonding between Pt and these oxygen anions is through an electrical double layer at the Pt surface which affects the work function of metal as reported by [Yamamoto *et al.* (1980)]. The total voltage response (ΔV) or change in electrical potential across the dipole layer in gridded structure is to be given by the following equation:

$$\Delta V = \gamma_i \Delta V_i + \gamma_b \Delta V_b + \gamma_d \Delta V_d + \gamma_{os} \Delta V_{os} + \gamma_{is} \Delta V_{is}$$

Where, γ is the function of temperature or metal coverage. From the above equation it is evident that the voltage response is the sum of responses at metal-dielectric interface (i), on the metal surface along the borders of the cracks (b), exposed surface of dielectric (d), outer side wall (os) and inner side wall (is) [Soo *et al*. (2010)]. The last term ($\gamma_{is}\Delta V_{is)}$ represents the voltage response due to inner side wall in gridded structure. This term is additional in gridded structure as compared to ungridded structure which is the main cause to increase the sensitivity of this structure.

Solomonsson *et al*. [Solomonsson *et al*. (2005)] reported that Pt-MIS sensor shows approximate one third sensitivity value for H_2 as compared to that of the Pd-MIS sensor. In spite of this, in the present study Pt gate sensor has shown better sensitivity

towards the H_2 as compared to Pd/TiO_2/Si and Pd/SiO_2/Si MOS sensors reported by earlier researchers [Yadava *et al*. (1990); Pandey *et al*. (2009 (a&b))].This improvement in sensitivity is attributed to gridded gate structure of Pt gate MOS sensor, which is the uniqueness and innovation in this study. As far as the available literatures and to the best of authors' knowledge, gridded Pt/SiO_2/Si MOS sensor has been fabricated for the first time and exclusive study has been done for the detection of H_2 and H_2 containing gases.

4.5 Conclusions

The gridded Pt gate MOS structure has been fabricated for H_2 and H_2 containing gas detection and observed improved sensitivity towards these gases. The sensor is more selective for H_2. It shows better sensitivity to H_2 (~90%) as compared to other test gases at low frequency (15 KHz) as compared to high frequency (25 KHz and 50 KHz). which is due to the higher activation energy and dissociation potential of H_2 as compared to other test gases. Although, this sensor does not respond to H_2S at room temperature, which is due to the low activation energy and dissociation potentials of H_2S at room temperature [Weixin and Yibing (1988)]. Further it has been concluded that gridded gate MOS sensor can detect low concentration of NH_3 (25 ppm), CH_4 (50 ppm) and H_2S (10 ppm). It has been found that gridded Pt/SiO_2/Si MOS structure shows higher sensitivity to H_2 which is found to be higher as reported by earlier researchers [yadava *et al*. (1990); Pandey *et al*. (2009(a&b))]. The higher sensitivity of gridded Pt/SiO_2/Si MOS structure to these test gases (H_2, NH_3, CH_4 and H_2S) in air is attributed to the side diffusion of H_2 molecules, increase in fixed charge density, spillover effect of H_2 molecules, increase in surface area caused by gridded structure, large porosity found in Pt gate film and decrease in interface trap charge density with concentration of test gases. It is also concluded that low frequency G-V response is better as compared to high frequency since it provides more accurate information regarding interface trap charges. Better response at lower frequency may be due to the balanced communication of H_2 generated interface traps with valance and conduction band of silicon substrate [pandey *et al*. (2009(b))]. Thus, it is concluded that gridded structure may be a preferred choice for detection of low concentration of NH_3, CH_4 and H_2S.