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MOS sensor for detection of NH_3 and H_2 gases

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Due to the increased industrialization, emission of green house gases, environment protection becomes an important issue for earth. Therefore, it is necessary to monitoring and controlling of such pollutants by developing an electronic device which may be utilized as a portable detector.

The $Pt/SiO_2/Si$ MOS sensor was fabricated on p-type <100> Si wafer with thermally grown SiO_2 layer of thickness about 100 Å. The platinum (Pt) gate with thickness 350 Å was deposited by vacuum evaporation technique. This sensor is tested towards H_2 and NH_3. The effect of H_2 and NH_3 on C-V and sensitivity (s) of the sensor were measured at 25 KHz at room temperature. The sensor exhibited better sensitivity (80%) for both the gases, as compared to reported earlier. This sensor is capable to detect low concentration of H_2 and NH_3. The minimum concentration of NH_3 and H_2 is 50 ppm and 250 ppm respectively, at room temperature.

Keywords: MOS sensor, Pt, hydrogen, C-V characteristics, NH_3, H_2.

Introduction

The development of convenient and efficient device for detection of hydrocarbon-vapors (viz. ethanol, acetone, trichloroethylene (TCE) etc.), H_2S and NH_3 have received urgent demand in chemical and pharmaceuticals industries. Acetone oxidizes in air severely and thereby, depletes the oxygen contents of atmosphere playing as noxious air pollutant. TCE is a major ground water pollutant which is responsible for hazardous water borne diseases. Due to safety reasons, the monitoring and controlling of such pollutants has become an important issue[1]. Based on solid state device, the MOS sensor can be divided into three categories, i.e. capacitor, field effect device and Schottky diode. In the above said devices, the interface properties dominate the whole performance[2].

It is well known that molecular H_2 is dissociated, adsorbed and dissolved as atomic hydrogen by certain metals like Pd[3]. It was shown that some of the dissolved hydrogen atoms are adsorbed at Pd-SiO_2 interface, where they give rise to dipole layer. In most Si based H_2 detectors, fermi-level pinning effect is caused by the palladium silicide formation. Therefore, Si-based gas sensors are fabricated with a thin oxide layer[4–6]. However, greater the thickness of oxide layer, the lower the sensitivity of H_2 response for the surface contamination[7].

The first MOS gas sensor was fabricated by Lundstrom *et al.* in1975. It has been reported that sensors investigated with Pd layers from 100 to 1000 Å and oxide thickness from (30–1000 Å) exposed to hydrogen results in a change in the flat band voltage of the device and hence a shift in the C-V curves along X-axis (voltage)[8]. Kumar *et al.* showed the effect of R.F. plasma processing on the behavior of MOS sensor towards the hydrogen detection. They reported that the sensitivity increases if porosity in sensing layer increases[16]. Yadav *et al.*[9] have fabricated a $Pd/TiO_2/Si$ MOS capacitor sensor. They have reported that the fixed surface state density in such a device increases linearly upon exposure to hydrogen gas concentration. They have reported 47% sensitivity to hydrogen in nitrogen ambient atmosphere. Harris[10] has reported $Ti/TiO_2/Pt$ MOS sensor for hydrogen detection. The detection of hydrogen was based on change in conductance of TiO_2. Pandey *et al.*[11,12] have reported the C-V characteristics and sensitivity vs bias voltage characteristics for the $Pd/SiO_2/Si$ MOS capacitor following exposure to hydrogen and methane. They have reported the 73% sensitivity to hydrogen. In this paper we reported the influence of hydrogen and NH_3 on C-V characteristics and sensitivity of the Pt gate MOS capacitor sensor, exposed to various concentrations of hydrogen in air at room temperature. The fabricated

MOS sensor showed better sensitivity (~85%) as reported earlier[9,10,12]. The following are the relevancies of MOS sensor to detect the toxic and hazardous gases (i) highly sensitive to NH_3, H_2, H_2S etc., (ii) small in size (upto few μm), (iii) cost effective, (iv) operated efficiently upto 180°C and (v) fast response and recovery time (approximately 65 s and 32 s respectively)[13].

Experimental

The front side of the wafer is spin coated with negative photoresist using the spinner and then the wafer is prebaked for 10 min at 90°C. After prebaking, a standard mask of required gridded gate structure is kept on the upper surface of silicon wafer then the surfaces (coated with photoresist) is exposed to UV light for 2 min which hardens the photo-resist under the transparent part of the mask. Then the photoresist is developed in the developer and unexposed photoresist is dissolved. Now, the wafers is post baked in the oven for about 20 min at 150°C. The complete lithographic process is carried out in the yellow room. A standard mask which is used to form gridded gate structure. The outer and inner diameters of gate structure were kept 1 mm and 0.2 mm, respectively. Aqua regia (HNO_3 + HCl = 1:3) is used for Pt metal etching. Subsequently, the photo-resist from the front side is removed by chemical etching (using the solution consisting of acetic acid + TCE + acetone : 5:20:10).

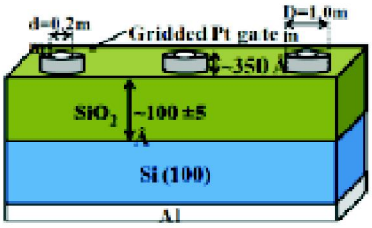

Fig. 1. 3D structure of grided Pt gate MOS sensor[14].

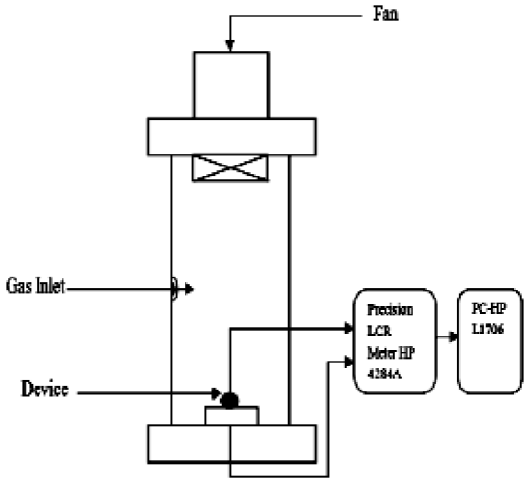

Fig. 2. Experimental setup for C-V measurement of MOS sensor[14].

Results and discussion

The C-V measurements of the fabricated grided gate MOS capacitor have been carried out in air, in a closed chamber upon exposure to different concentrations of H_2 (250–2000 ppm) and NH_3 (50–700 ppm) at 25 KHz frequency. The experiment is performed at room temperature. The C-V response of fabricated MOS capacitor sensor is depicted in Fig. 3 and Fig. 4 for both the gases. The C-V curve shifts

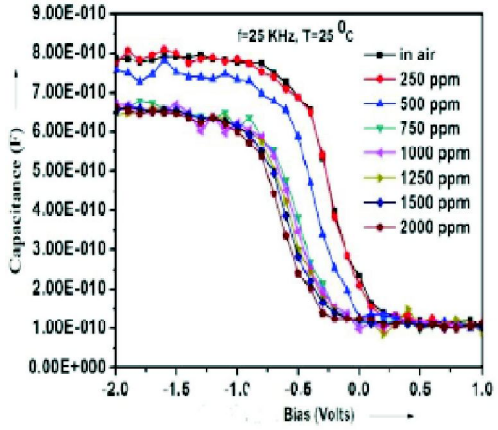

Fig. 3. Capacitance vs voltage (C-V) response of Pt gate MOS sensor at various concentration of H_2 at room temperature at *f* = 25 KHz.

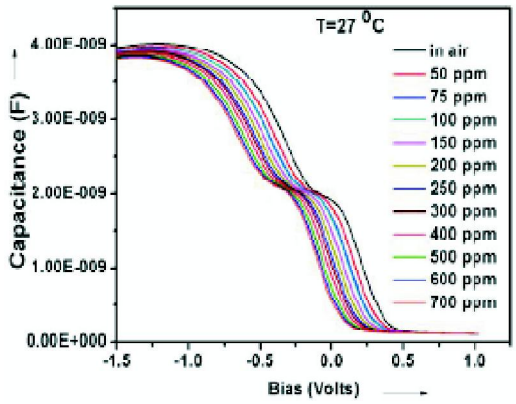

Fig. 4. Capacitance vs voltage (C-V) response of Pt gate MOS sensor at various concentration of NH_3 at room temperature at *f* = 25 KHz.

towards the negative side of the voltage axis as well as concentration of the H_2 and NH_3 gas is increased. It is observed that as the concentration of H_2 and NH_3 increases capacitance decreases and the sensitivity of the sensor increases. The decrease in capacitance continues till saturation comes. The variation of sensitivity of the sensor with bias voltage for various concentrations of H_2 and NH_3 is shown in Fig. 5 and Fig. 6.

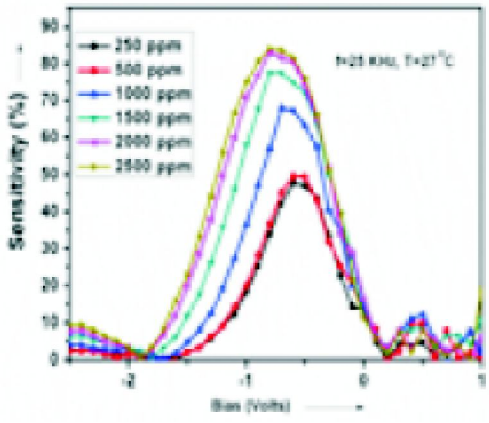

Fig. 5. Sensitivity vs bias voltage for various concentrations of hydrogen at room temperature at f = 25 KHz.

The sensitivity of a sensor is given by

$$\text{Sensitivity } (s)\ \% = \frac{\Delta C \times 100}{C}$$

where C is the capacitance in air, ΔC is the change in capacitance at a certain gas concentration.

Lundstrom[8] and Shivaraman *et al.*[15] observed that the shift in C-V corresponds to the change in flat band voltage is

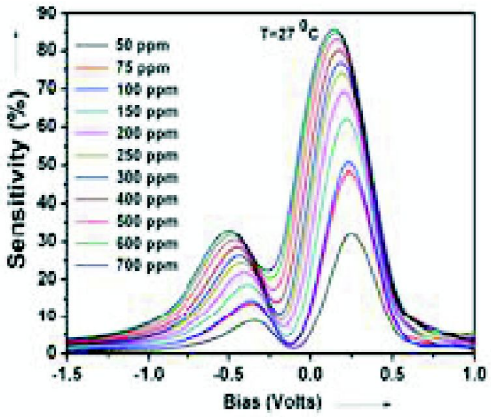

Fig. 6. Sensitivity vs bias voltage for various concentrations at room temperature at f = 25 KHz.

attributed to creation of dipole layer due to adsorbed hydrogen at Pd/SiO_2 interface. The change in V_{FB} is evaluated by the following researchers[9]. It has been proposed that when catalytic gate (Pd, Pt etc.) MOS structure is exposed to hydrogen, the hydrogen molecules are first dissociated into atoms due to catalytic behavior of Pd/Pt and then these atoms are adsorbed on the metallic gate surface. Subsequently some of the H_2 atoms diffuse through the metallic film and are adsorbed onto the metal/insulator interface. These atoms are polarized and give rise to the dipole layer. The presence of the dipole layer changes an effective work function of platinum. Due to more porous structure of Pt film, results in high polarization of SiO_2 layer and give rise to dipole layer which effectively changes the work function of Pt film. Hence, the device performance is improved (i.e. high sensitivity and low response recovery time). Due to high sensitivity this sensor can be tested for other gases like CH_4 and C_2H_2 etc.

Table 1. Comparison between gridded gate MOS sensor vs others

Sl. No.	Type of sensor	Sensing layer	H_2			NH_3			Ref.
			% Max. concentration	% Sensitivity	Temp. (°C)	% Max. concentration	% Sensitivity	Temp. (°C)	This
1.	$Pt/SiO_2/Si$ gridded gate	SiO_2	0.2 (2000 ppm)	80	Room	0.07% (700 ppm)	85	Room	sensor
2.	$Pd/TiO_2/Si$	TiO_2	4	51	Room	No data	–	–	17
3.	$Pd/SiO_2/Si$	SiO_2	8	30	Room	No data	–	–	12
4.	$Pd/TiO_2/Si$	TiO_2	8	47	Room	No data	–	–	9
5.	$Pd/SiO_2/Si$	SiO_2	0.35 (3500 ppm)	73	Room	No data	–	–	11
6.	MoS_2 film based	MoS_2	No data		No data	400	40	80	18

Conclusion

It is concluded that Pt gate MOS capacitor sensor with porous gate structure shows high sensitivity to hydrogen and NH_3 (>80%) both. It is believed that due to more porosity in the metallic gate (Pt) high polarization of SiO_2 occurs which gives rise to the formation of strong dipole layer at metal/ insulator interface, the porous gate structure results in the change of surface state density. When we expose the MOS sensor to hydrogen gas in an ambient atmosphere of air, it reacts with oxygen atoms on the interface and a decrease in the concentration of negatively charged ions takes place. This results in decrease in surface state density and hence a shift in C-V characteristics, which ultimately leads to increase in sensitivity[16].

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