CHAPTER 4

Room-Temperature Hydrogen Sensing Properties of Electron Beam Evaporated TiO_2 Thin Film Based MOS Device*

Contents

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CHAPTER 4

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4.1 Introduction

It is shown in Chapter-3 that the thermally evaporated TiO_2 thin film based Pd/TiO_2/Si/Al MOS sensor has a high hydrogen response at room temperature. It is discussed in Chapter-1 that the structural, chemical, electrical, and optical properties of the thin films are dependent on the deposition technique also [Alferov (2001), Chen, and Mao (2007), Paul, and Giri (2017)]. That is why the sol-gel TiO_2 thin films did not show room-temperature hydrogen sensing in Chapter-1 while the thermally evaporated TiO_2 showed good hydrogen sensing properties discussed in Chapter-3.

It is found that the thin film deposited by the electron beam evaporation (EBE) method has a regular nanostructure with good quality and purity [Lokhande *et al.* (2016)]. The EBE technique also provides a high deposition rate among all evaporation techniques. This chapter thus investigates the room-temperature sensing property of the electron beam evaporated TiO_2 thin films in the MOS sensor structure considered in Chapter-3. The Pd electrode on the TiO_2 film acts as a catalyst for hydrogen atom diffusion to get adsorbed at the metal/oxide interface. Thus a dipole layer is formed, and this dipole layer subsequently changes the work function of Pd metal [Pandey *et al.* (2009), Luo *et al.* (2017)]. The fabricated MOS sensor has a very fast response and high sensitivity for hydrogen gas in an ambient atmosphere as well as a nitrogen environment operated at room temperature. The outline of the rest of this chapter is:

Section 4.2 discusses the experimental details for fabricating the electron beam evaporated TiO_2 film-based Pd/TiO_2/Si MOS sensor. Section 4.3 provides some important results related to the surface and structural morphologies of the fabricated Pd/TiO_2/Si MOS sensor and EBE TiO_2 films. The performance of the proposed MOS sensor has been compared with that of the sol-gel derived spin-coated MSM sensor discussed in Chapter 2 and thermally deposited TiO_2 nanostructured based Pd/TiO_2/Si/Al metal oxide semiconductor (MOS) sensor discussed in Chapter 3. Finally, Section 4.4 concludes the major finding and observations of this chapter.

4.2 Experimental Details

In this section, thin film deposition and fabrication steps using for fabricating the electron beam evaporated TiO_2 based Pd/TiO_2/Si MOS sensor for hydrogen detection are presented.

4.2.1 Materials and Sensor Fabrication

The p-Si (100 orientation and 2–7 Ω.cm resistivity) is used as a substrate and semiconducting material for device fabrication. The rectangular substrates of 25 mm × 20 mm size are cleaned using the wet chemical method as already discussed in Chapter 2. The small part of TiO_2 pellets (10 mm diameter and 2 mm thick) is used as the evaporating material in the electron beam evaporation (EBE) unit (Model No. FL400 SMART COAT 3.0 A from Hind HiVac, Bangalore, India) [Rawat *et al.* (2016)]. TiO_2 is deposited at a vacuum of $\sim 2\times10^{-6}$ mbar and a deposition rate of ~0.1 nm/s to obtain the ~10 nm thin TiO_2 film on the cleaned p-Si substrates. The obtained TiO_2 film on p-Si substrates is then annealed at 500°C for 30 minutes in the ambient air atmosphere using the annealing furnace (from Thermco, USA). Further, the Pd dots of 2 mm diameter and ~40 nm thin are deposited at a rate of ~0.5 nm/s over TiO_2 film by the

EBE method using a shadow masking technique. Note that Pd metal thickness above ~30 nm is sufficient for establishing good electrical contact on the TiO_2 films [G. J. Maclay. (1985)]. For the bottom contact, 100 nm thin aluminum film is deposited on p-Si using thermal vacuum deposition (Model No. FL400 SMART COAT 3.0 A from Hind HiVac, Bangalore, India). Finally, the fabricated MOS sensors are annealed at 450°C in the nitrogen atmosphere for 7 minutes. The device structure of the as-fabricated MOS sensor is shown in Figure 4.1 (a).

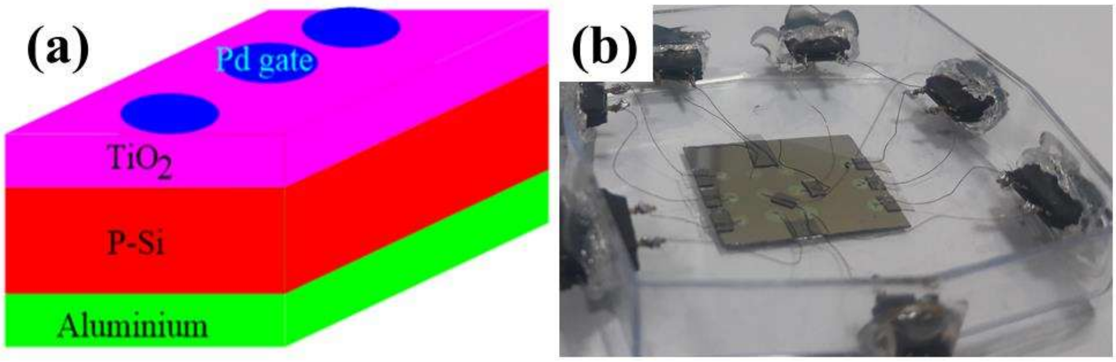

Figure 4.1: (a) Device structure of the MOS sensor and (b) Packaged MOS sensor.

For the capacitance and conductance measurements of the fabricated MOS sensor, it is first packed in an acrylic box, and its Pd and Al metal pads are then connected to a fine copper wire of 0.1 mm diameter using high-quality silver paste. Finally, the electrical soldering technique is used to connect the copper wire with the pin of the PCB female header, as shown in Figure 4.1 (b).

4.2.2 Film and Sensor Characterizations

The surface morphology of deposited TiO_2 film and Pd film have been investigated by atomic force microscopy (AFM) (scanning probe microscopy, Model No. NTEGRA Prima, NT-MDT Services and Logistics Ltd., Ireland) and scanning electron microscopy (SEM) (Model: EVO MA 15/18, from Carl Zeiss Microscopy Ltd., UK).

The elemental composition of the film is investigated by energy-dispersive x-ray spectroscopy (EDS) (from Oxford, UK). The capacitance-voltage (*C*-*V*) and conductance-voltage (*G*-*V*) characterizations are done using a semiconductor parameter analyzer (Model B1500A from Keysight). The gas sensing measurements are carried out in a homemade gas sensing chamber (already discussed in Chapter 1). The various concentrations of hydrogen gas and organic vapors are injected into the gas chamber, and the respective changes in capacitance and conductance have been measured.

4.3 Results and Discussion

In this section, the electron beam evaporated TiO_2 based Pd/TiO_2/Si MOS sensor thin film, electrical, and hydrogen gas sensing characterization are discussed.

4.3.1 Thin Film Surface Characterization

The nano-level roughness is observed in the TiO_2 film, and Pd dots on TiO_2 film measured from AFM images, as shown in Figure 4.2. The roughness parameters obtained from the AFM analysis of TiO_2 film and Pd dots are listed in Table 4.1.

Table 4.1: Surface parameters for deposited TiO_2/Pd films.

Parameters/Film	TiO_2	Pd
Average roughness (nm)	0.1	2.2
RMS roughness (nm)	0.2	2.9
Peak to peak spacing (nm)	1.9	31.9

These smaller roughness parameter values for TiO_2 obtained from the AFM image shown in Figure 4.2 (a) confirm very smooth and uniform TiO_2 film on silicon. However, the larger values of roughness parameters for Pd dots obtained from the AFM image shown in Figure 4.2 (b) confirm the porosity in the Pd film.

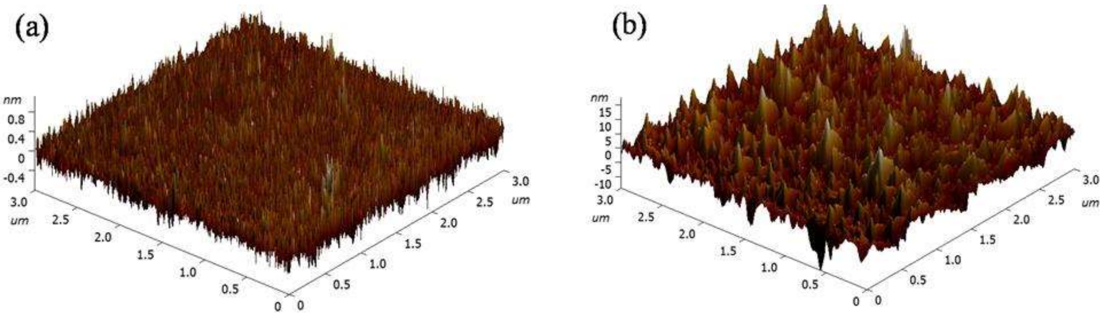

Figure 4.2: AFM image of (a) TiO_2 film on p-Si and (b) Pd dots on p-Si/TiO_2 film.

The surface morphology of Pd dots on TiO_2 film is obtained from SEM, as shown in Figure 4.3. Discontinue and cracks like surface morphology is obtained for Pd dots, which is also supported by our AFM data [Pandey *et al.* (2011)]. These porous surfaces, due to cracks, enhance the gas adsorption through Pd film [Erdem *et al.* (2016)].

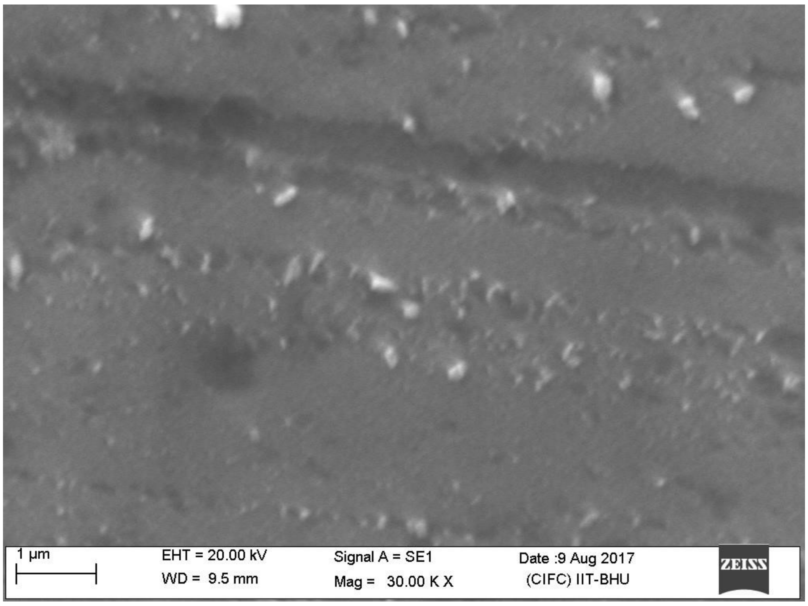

Figure 4.3: SEM image of Pd dot on TiO_2 film deposited on a silicon substrate.

The elemental compositions for the Pd dot on the TiO_2 film obtained from EDS are shown in Figure 4.4, while position mapping is shown in the inset. The elemental analysis confirms the presence of titanium, silicon, oxygen, and palladium. The small peaks of titanium, oxygen, and palladium are due to the very thin film of TiO_2 and palladium as compared to silicon.

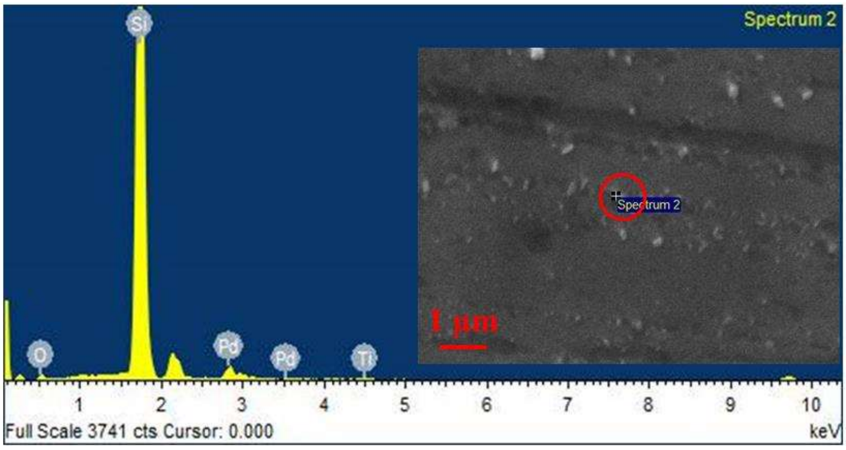

Figure 4.4: EDS image of Pd dot on TiO_2 film deposited on the silicon substrate, while the inset shows the position of mapping.

4.3.2 Electrical Characterization of MOS Sensor

The fabricated MOS sensor is electrically characterized at room temperature (23°C), relative humidity (RH) of 60%, and in an ambient air atmosphere. The capacitance-voltage (*C*-*V*) and conductance-voltage (*G*-*V*) characterizations have been carried out at various frequency ranges from 200 kHz to 1 MHz in an ambient atmosphere as shown in Figure 4.5 (a) and Figure 4.5 (b). It is found that the capacitance and conductance are high at lower frequency whereas low for the higher frequency in a particular voltage range. The capacitance and conductance are inversely proportional to frequency, so its value decreases as frequency increases.

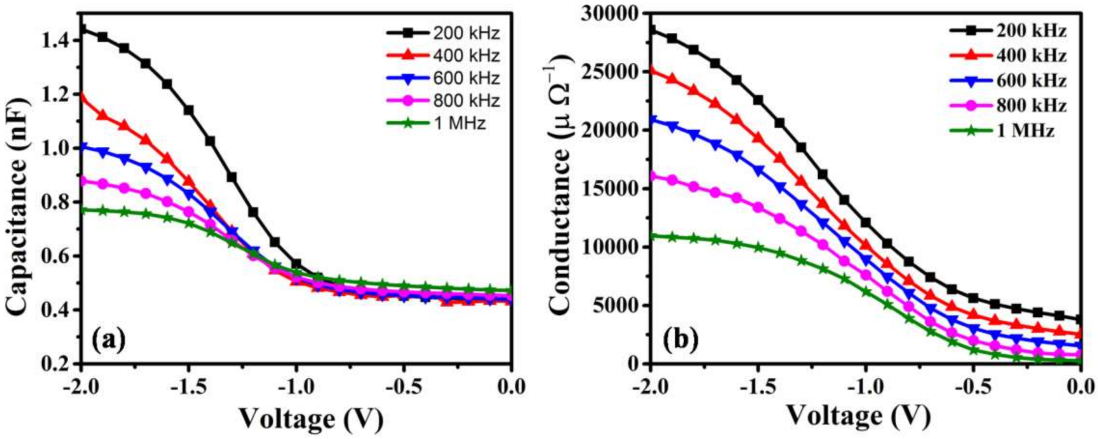

Figure 4.5: (a) *C*-*V* and (b) *G*-*V* characteristics of MOS sensor at a different frequency.

4.3.3 Hydrogen Sensing of MOS Sensor

The fabricated MOS sensor is exposed to various concentrations of hydrogen gas in the gas sensing chamber in an ambient atmosphere. In general, we have observed a lower capacitance with higher hydrogen gas sensitivity at higher frequencies, as also observed by others [Dwivedi *et al.* (2000)]. In view of the above observation, we have carried out all the measurements of our MOS sensor characteristics at 1 MHz frequency. The change in capacitance and conductance at the 1 MHz frequency due to exposure of hydrogen gas are shown in Figure 4.6 (a) and Figure 4.6 (b), respectively.

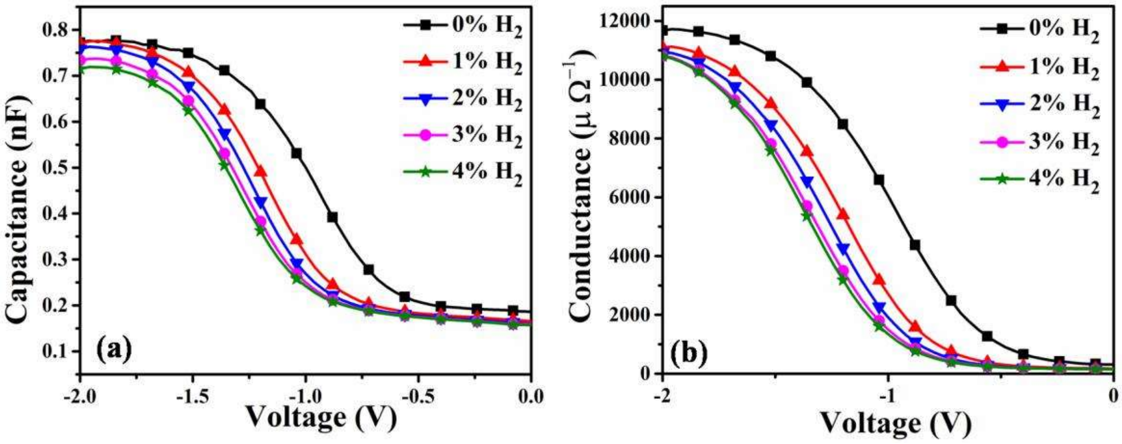

Figure 4.6: (a) *C*-*V* characteristics and (b) *G*-*V* characteristics at 1 MHz frequency of MOS sensor for the various concentration of H_2 gas.

It is found that with the increase in hydrogen gas concentration, both the capacitance and conductance are decreased. The capacitance and conductance are saturated for higher hydrogen gas concentration. The change in capacitance or conductance is due to the adsorption of hydrogen gas through palladium dots. Palladium is a noble metal, and it works as an active site on the TiO_2 layer, which is very helpful in the adsorption of the target gas. In this fabricated sensor, Pd dots offer a reaction pathway that can reduce the activation energy, to enhance the reaction rate, sensitivity, selectivity, and reliability [Adams *et al.* (2010)]. When H_2 gas is exposed to this fabricated sensor, firstly, H_2 molecules dissociate into H (active species) in the presence of Pd. After this, active species H spill-over and adsorbed to the surface of metal oxide [B. Liu *et al.* (2014)]. It may also be mentioned that despite some differences in the pattern of the discontinuities or cracks on the surface of different Pd dots (see Figure 4.3), nearly similar *C-V* and *G-V* characteristics under H_2 exposure have been observed for all the Pd dots.

The fabricated MOS sensor under hydrogen gas exposure has two type of charges: one is due to chemisorptions of oxygen, which is called oxide trap charge [Yamamoto *et al.* (1980)], and another is fixed oxide charge, which is trapped at TiO_2/Si interface [Deal (1980)]. When H_2 gas is exposed to a fabricated MOS sensor, there is a reaction between TiO_2 and H_2 along with a polarized hydrogen atom layer formed at Pd/TiO_2 and TiO_2/Si interface. These reactions are responsible for the voltage drop, which also change the flat-band voltage (V_{FB}) of the MOS, and a shift in *C-V* characteristics occurs [Yadav *et al.* (2007)]. The shift in *C-V* is more towards negative voltage, and this is due to a change in the flat band voltage of the device after exposed to H_2 gas. The flat band voltage (V_{FB}) of the MOS device can be written in terms of surface charge density (Q_{SS}), work function difference between the metal and semiconductor (φ_{ms}), and insulator capacitance (C_i) as [Yadava *et al.* (1990)]:

$$V_{FB} = \varphi_{ms} - \frac{Q_{SS}}{C_i} \tag{4.1}$$

The surface state density linearly increases with the increase in the hydrogen concentration but with the decrease in the thickness of the oxide layer [Yamamoto *et al.* (1980), Yadava *et al.* (1990)]. On the other hand, the adsorption of hydrogen in the Pd changes the work function of Pd and hence the value of φ_{ms} . The combined effects of changes in the surface state density and work function difference shift the flat band voltage towards a more negative side [Poteat and Lalevic (1981)]. Since the ratio of Q_{SS} and C_i is the maximum near -1 V, we observe the maximum shift in the flat band voltage at -1 V. The very small thickness of ~10 nm of the TiO_2 oxide layer in our fabricated MOS sensor is considered to make the device highly sensitive for hydrogen gas. However, the oxide thickness below ~10 nm may cease to maintain the MOS action due to the dominant carrier tunneling phenomenon.

4.3.4 Sensitivity of MOS Gas Sensor

The sensitivity is the key parameter that determined the range and usability of the sensor for specific level gases [Pandey *et al.* (2009), C. Kumar *et al.* (2017)]. The sensitivity of the MOS sensor is defined as the percentage ratio of change in capacitance (or conductance) to the initial capacitance (or conductance). It is mathematically expressed as follows:

$$\begin{aligned} Sensitivity\,(\%) &= \frac{\Delta C}{C} \times 100 \\ &= \frac{\Delta G}{G} \times 100 \end{aligned} \tag{4.2}$$

Where, ΔC and ΔG is the change in capacitance and conductance, respectively, due to exposure of H_2 gas. C and G is initial capacitance and conductance, respectively, under unexposed to hydrogen gas condition. It is observed that the capacitance and conductance are decreased with the increase in hydrogen gas concentration but get saturated at the higher concentrations. The capacitance vs. hydrogen concentration and conductance vs. hydrogen concentration characteristics for a fixed applied bias of -1 V are plotted in Figure 4.7 (a). The sensitivity is calculated using Eq. (4.2) from the change in capacitance or conductance, and the characteristics of sensitivity vs. hydrogen concentration are plotted in Figure 4.7 (b). It is observed that the change in conductance is higher than the change in capacitance. Thus, the sensitivity calculated from conductance is higher than the capacitance.

The sensitivity of the MOS sensor for 4% of hydrogen gas in the ambient air and N_2 atmosphere is calculated using Eq. (4.2) and plotted in Figure 4.8 in the voltage range of -2 V to 0 V. When the MOS sensor is tested under ambient air atmosphere, a part of the exposed hydrogen gas is wasted due to its reaction with the oxygen of the ambient air

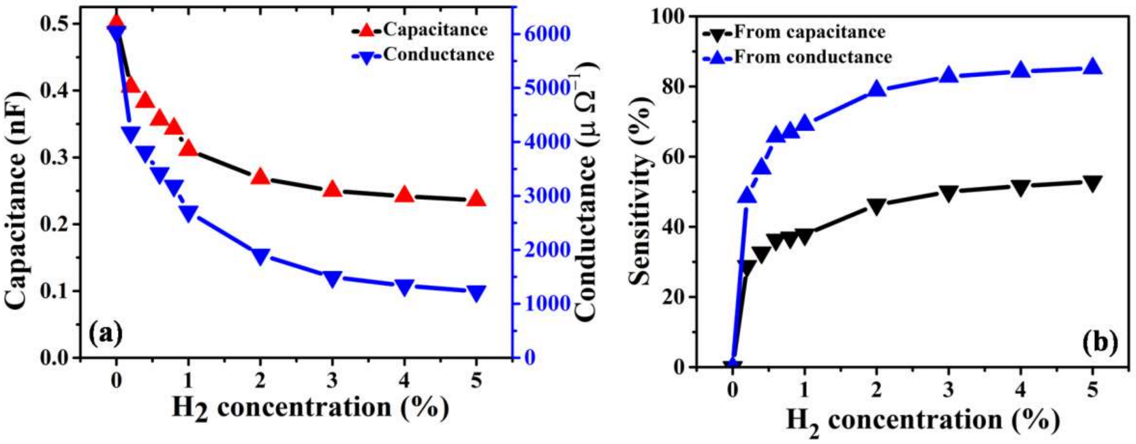

Figure 4.7: (a) Capacitance and conductance vs. H_2 concentration and (b) Sensitivity vs. H_2 concentration.

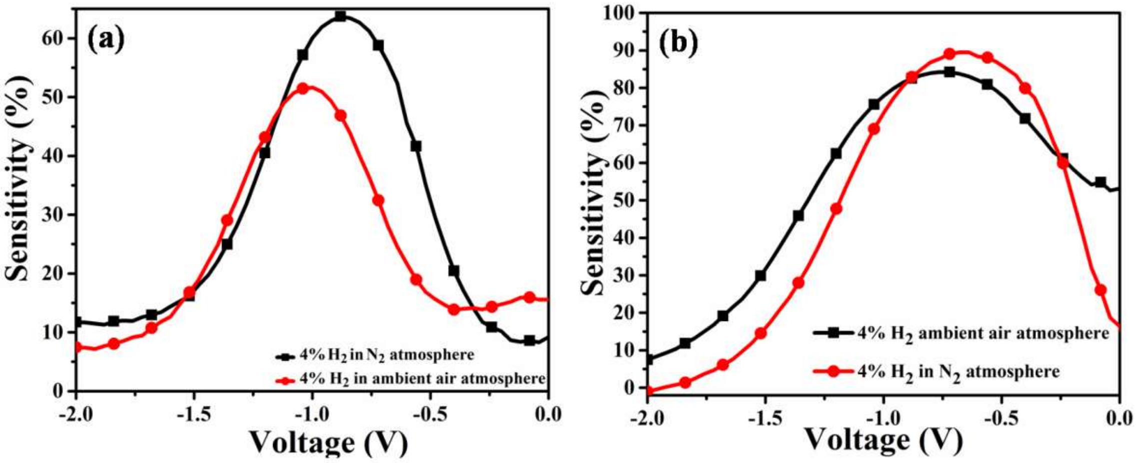

Figure 4.8: Sensitivity vs. applied voltage at 4% concentration of H_2 gas in ambient air and nitrogen atmosphere calculated from (a) capacitance and (b) conductance.

covered on the Pd dots [Heiland (1981)], and the remaining gas reaches the oxide for adsorption. However, due to the inert nature of the N_2 gas, direct hydrogen dissociation can take place under the N_2 environment so that the ionized hydrogen atoms can reach the oxide surface for adsorption [Heiland (1981), Moon *et al.* (2016)]. This results in a larger change in capacitance of the sensor (under hydrogen exposure) in an N_2 environment than that measured under ambient air atmosphere. In other words, a higher sensitivity of the fabricated MOS sensor is measured under an N_2 atmosphere than that measured in the ambient air condition. The maximum sensitivity of 51% in the ambient atmosphere and 64% in the nitrogen atmosphere is obtained using a change in capacitance. However, the maximum sensitivity calculated from conductance is 84% in ambient air and 90% in the N_2 atmosphere. The response time and recovery time are defined as the time taken by the sensor to achieve 90% of the total change in the capacitance after gas exposure and gas removal, respectively [Wu *et al.* (2013), C. Kumar *et al.* (2018)]. The obtained values of the response and recovery times for 4% hydrogen gas in an N_2 environment are ~52 s and 48 s, respectively.

4.3.5 Selectivity of MOS Sensor

Since the humidity is considered to affect the performance of the gas sensors [C. Kumar *et al*. (2018)], we have measured the gas response and sensitivity under different relative humidity conditions. The variation in the relative humidity (RH) is achieved by the circulation of dry air in the gas chamber in the presence of silica gel. The capacitance is found to be negligibly decreased with the increase in the relative humidity. This is due to the formation of a very thin layer of water over the Pd dots, which slightly reduces the diffusion of hydrogen gas into the Pd dots and slightly decreases the change in capacitance with the increase in RH with 1% of error as shown in Figure 4.9. However, the sensitivity is found to be increased with decreased RH due to increased gas adsorption.

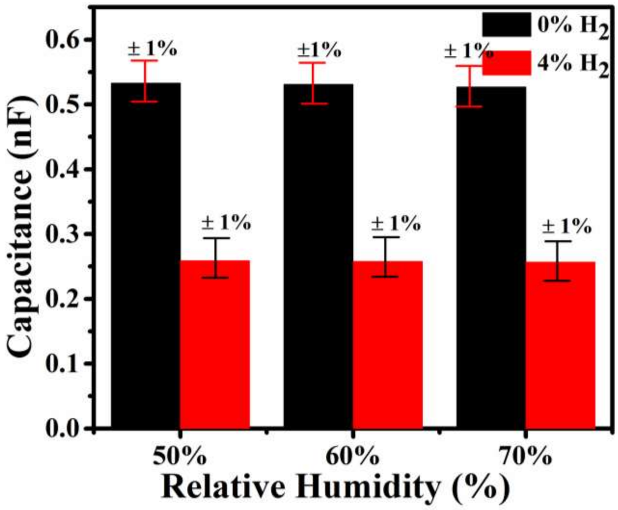

Figure 4.9: Capacitance vs. relative humidity for 0% and 4% H_2 at an applied voltage of -1 V.

The most common atmospheric interferences towards hydrogen gas sensors are organic vapors. The organic vapors such as acetone, chloroform, ethanol, isopropanol, and methanol are investigated for their interfering properties towards hydrogen sensing. 1% of all these vapors along with hydrogen gas are exposed to the MOS sensor, and corresponding sensitivities are compared, as shown in Figure 4.10. The corresponding error is ~2%.

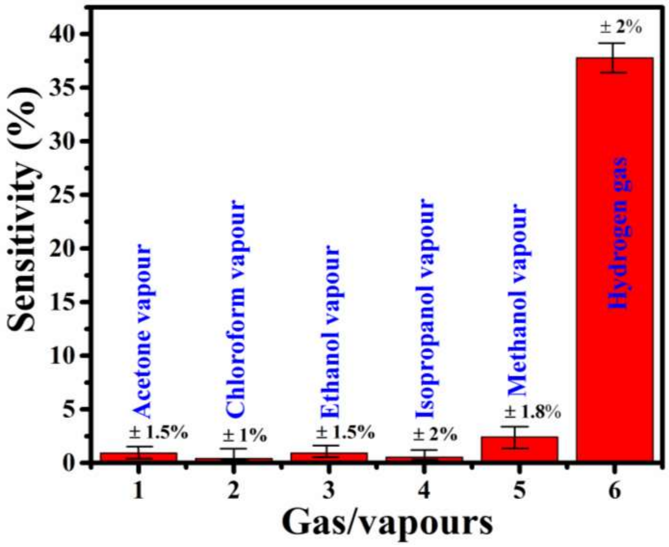

Figure 4.10: Selectivity characteristics of the hydrogen sensor in the presence of common interferences.

It is observed that the fabricated sensor is very less sensitive to organic vapors. Thus, the fabricated MOS sensor using electron beam deposited TiO_2 and Pd films have a high selectivity to the hydrogen gas due to selective adsorption of H_2 gas on Pd dots [Xiang *et al.* (2014)]. For the effect of the environment, we have investigated the selectivity of the sensors in the presence of various interference species generally found along with hydrogen gas. It is obvious from the selectivity characteristics that the hydrogen responses are not affected by the interference species present in the harsh environment. The sensing performance of our TiO_2 based MOS sensor is compared with other reported Pd/Oxides/Si structure-based MOS capacitive sensors in Table 4.2. It is observed that the combination of EBE films of TiO_2 and Pd are best suitable for achieving the enhanced hydrogen gas sensitivity at room temperature.

Table 4.2: Comparison of the Oxide Based MOS Capacitative Sensor for Hydrogen gas.

Oxide materials	**Deposition method**	**Working temperature (°C)**	**H_2 concentration (%)**	**Max. sensitivity (%)**	**Ref.**
TiO_2	Thermal evaporation	RT	2-8	47	[Yadava *et al.* (1990)]
SiO_2	Plazma	RT	1.184	75	[Dwivedi *et al.* (2000)]
TiO_2	Thermal evaporation	RT	8	54	[Yadav *et al.* (2007)]
TiO_2	Sol-Gel	175	4	26.75	Chapter 2
TiO_2	Thermal evaporation	RT	4	84	Chapter 3
TiO_2	Electron beam evaporation	RT (23)	4	90	This work

4.4 Conclusion

The Pd/TiO_2/Si MOS sensor with 10 nm thin electron beam deposited TiO_2 is fabricated, and sensing of low concentration hydrogen gas at room temperature is investigated. After exposure to H_2 gas, a significant shift in *C-V* and *G-V* curves is observed. The shifts in *C-V* and *G-V* curves are due to the higher polarizability of TiO_2 lattice, reduced oxide thickness, and increase in surface charge density with exposed H_2 gas. The maximum sensitivities for 4% H_2 gas at room temperature are found as 51% and 64% in ambient air and nitrogen gas, respectively, using capacitance. The maximum sensitivities for 4% H_2 at room temperature are 84% in ambient air and 90% in nitrogen gas using conductance. Hence, we conclude that the Pd/TiO_2/Si MOS sensor with reduced oxide thickness is more capable of detecting the low concentration of H_2 gas at room temperature in the ambient atmosphere.