CHAPTER 3

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

Contents

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CHAPTER 3

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3.1 Introduction

The Sol-Gel derived TiO_2 thin film based MSM sensor with interdigitated electrode for detecting the hydrogen gas is investigated in Chapter-2. Though the Sol-Gel derived TiO_2 thin film based MSM sensor has shown a significant hydrogen gas response at a higher temperature (175ºC), however, it shows a negligible response at room temperature. It is already discussed in Chapter-1 that a room-temperature hydrogen sensor is highly desirable due to the explosive nature of hydrogen at higher temperatures [Liu *et al*. (2013)]. In general, a capacitive structure is found to be more suitable for hydrogen sensing at room temperature operation [Yadav *et al*. (2007)]. That is why, the present chapter is devoted to investigating the room-temperature hydrogen sensing properties of a Pd/TiO_2/Si/Al-based metal-oxide-semiconductor (MOS) structure with a thermally evaporated TiO_2 film as the active layer of the device. The thicknesses of the TiO_2 thin film (i.e., sensing layer) and the porous Pd film have been fixed by optimizing the deposition rate of the films for maximizing the H_2 gas response at room temperature. The electrical and gas sensing properties of the fabricated device have been studied. The outline of the rest of this chapter is as follows:

Section 3.2 presents the experimental details regarding the fabrication of the proposed Pd/TiO_2/Si/Al structure-based capacitive MOS sensor for room-temperature operation. Various results and discussion related to surface and structural morphologies of the deposited films as well as electrical and hydrogen gas sensing properties of the fabricated device are presented in section 3.3. Finally, section 3.4 summarizes the major findings and observations of this chapter.

3.2 Experimental Details

3.2.1 Thin Film Deposition and MOS Fabrication

For fabricating the capacitive hydrogen sensor first, the p-type semiconducting silicon (p-Si) substrate (~375 µm thick, <100> orientation, and 2-7 Ω-cm resistivity) of about 25 mm × 20 mm size were taken. The standard wet cleaning process already discussed in Chapter 2 and also reported by Rawat *et al*. (2015) was used. Cleaned silicon substrates were loaded in the chamber of the thermal evaporator (Model No. FL400 SMART COAT 3.0 A from Hind High Vacuum, India) for the deposition of TiO_2 at a vacuum of $\sim 2\times10^{-6}$ mbar. An optimized thickness of 50 nm thin TiO_2 film was achieved on silicon substrates using a controlled deposition process. After deposition of TiO_2 thin film, the samples were annealed at 500°C for 30 minutes in a muffle furnace (from Thermco, USA) at ambient air atmosphere for achieving improved crystalline structure of the film [Rawat *et al*. (2015)]. For top contact, a porous 40 nm thin film of Pd metal is deposited as dots with a 2 mm diameter on the TiO_2 surface using a shadow masking technique in the thermal deposition unit. Later, for bottom contact, a 100 nm thin film of aluminum (Al) on the back of silicon is deposited. The deposition rates used for all the materials for the thermal evaporation are included in Table 3.1.

Table 3.1: Deposition rate for the thermal evaporation.

Material	Deposition rate (nm/s)
TiO_2	0.1
Pd	0.5
Al	0.4-0.5

Finally, the fabricated MOS device was annealed at 450°C for 7 minutes in the nitrogen environment. The block diagram of the complete MOS capacitor is shown in Figure 3.1 (a), and the camera image of the top of the final film is shown in the inset of Figure 3.1 (a). The fabricated MOS sensor is packaged for standalone use in the acrylic plastic case, 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 the camera (real) image in Figure 3.1 (b).

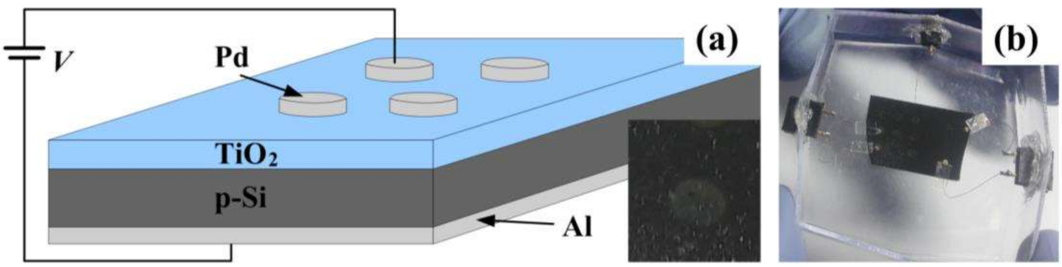

Figure 3.1: (a) Device structure of fabricated MOS sensor and the camera image of the top surface of the final film. (b) Camera (real) image of fabricated MOS devices on the p-Si substrate packaged in a plastic case.

3.3 Results and Discussion

In this section, first thin film characterizations and then electrical as well as gas sensing responses of Pd/TiO_2/Si/Al structure-based MOS capacitor sensors are presented and discussed in detail. The surface roughness, morphology, and the elemental composition of the deposited TiO_2 thin film were measured using NaioAFM (from Nanosurf, Switzerland), High resolution scanning electron microscopy (HRSEM) (Model: EVO MA 15/18, from Carl Zeiss Microscopy Ltd., Uk) and the energy-dispersive X-ray spectroscopy (EDS) (from Oxford, UK). The capacitance-voltage (C-

V) characteristics were investigated using a semiconductor parameter analyzer (Model B1500A from Keysight, USA).

3.3.1 Thin Film Characterization

The scanned surface of the TiO_2 thin film measured using NaioAFM in non-contact dynamic mode is shown in Figure 3.2. The surface roughness is calculated under the van der Waals force between the tip and surface of the sample. It is clear from the NaioAFM image that the thermally deposited TiO_2 thin film is highly uniform with nano-level roughness. The measured surface parameters such as average roughness, root mean square (RMS) roughness are listed in Table 3.2.

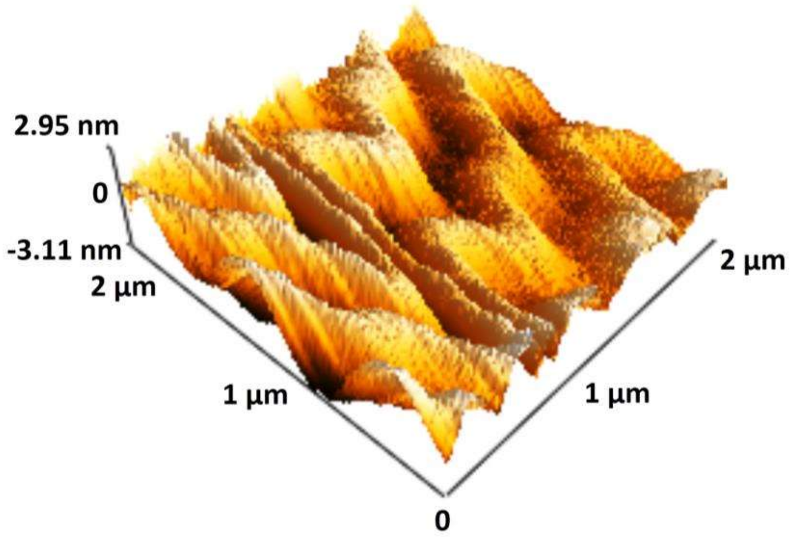

Figure 3.2: AFM image of 50 nm thin TiO_2 film on the p-Si substrate.

Table 3.2: Surface parameters for deposited TiO_2 films.

Parameters/Film	TiO_2
Average roughness (nm)	0.85
RMS roughness (nm)	1.04

The obtained nano-level roughness is considered to be useful for the enhanced sensitivity towards the exposed gases [C. Kumar *et al*. (2017)]. The surface roughness results in an increased reactive area for the exposed gas molecules on the surface of the film. Further, the surface morphology of thermally deposited TiO_2 obtained by HRSEM measurement is shown in Figure 3.3.

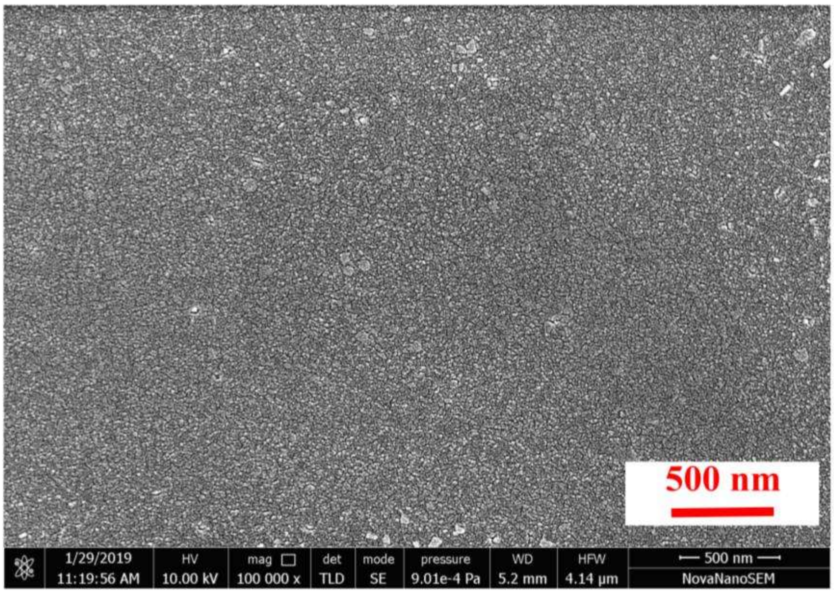

Figure 3.3: SEM image of TiO_2 film deposited on the p-Si substrate.

The HRSEM image is obtained by raster scanning through secondary electron or backscattered electron. The obtained surface morphology confirms that the grown film is of high purity and uniformity. The elemental composition in the deposited thin film and Pd dot is shown in Figure 3.4. The EDS data confirms the presence of titanium (Ti), oxygen (O_2), silicon (Si), and palladium (Pd) in Si/TiO_2 thin film. The peak for the silicon is due to underneath the silicon substrate.

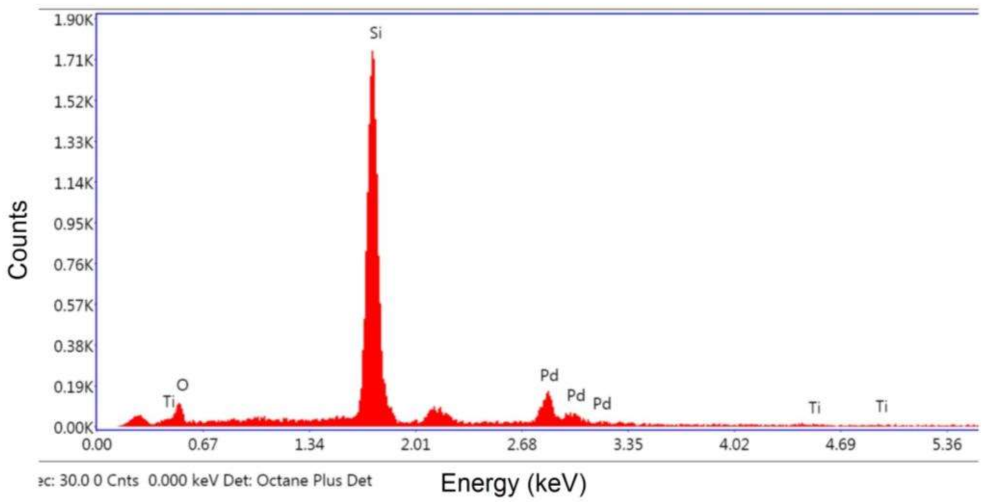

Figure 3.4: EDS image of TiO_2 thin film on the p-Si substrate.

3.3.2 Electrical Characterization

All the electrical and hydrogen gas sensing characteristics of the fabricated sensor are measured out at room temperature (23°C), relative humidity (RH) of 60%, and in the ambient air atmosphere operating conditions. The capacitance versus voltage (*C-V*) and conductance versus voltage *(G-V)* characteristics for the fabricated MOS sensor are measured at a frequency of 1 MHz. The gas sensing is performed inside a homemade self-design gas sensing chamber of volume 10 liters with inlet-outlet facilities, already discussed in Chapter 1 [C. Kumar *et al.* (2017)]. The change in the capacitance and the conductance for different concentrations of H_2 is shown in Figure 3.5 and Figure 3.6, respectively. The exposed hydrogen gas diffuses through the Pd thin film and interacts with TiO_2. The change in the capacitance and the conductance is mainly due to modification in the work function of Pd underexposure of H_2.

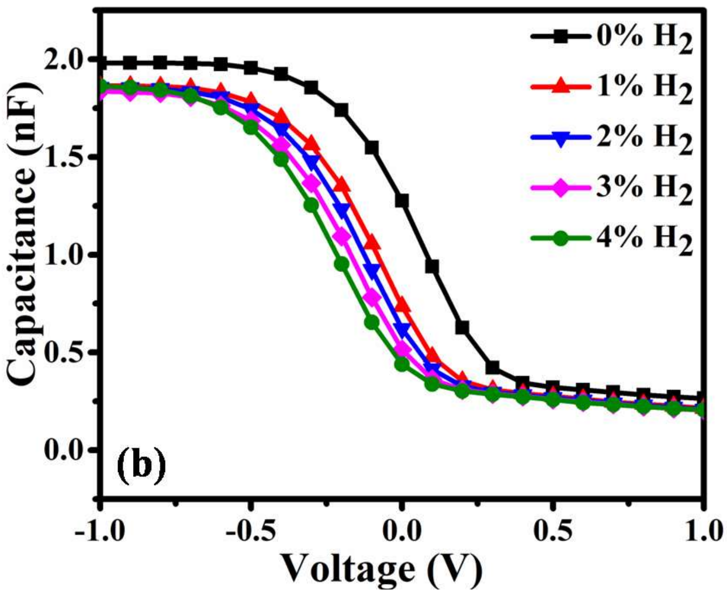

Figure 3.5: C-V characteristics at 1 MHz frequency for different concentrations of H_2.

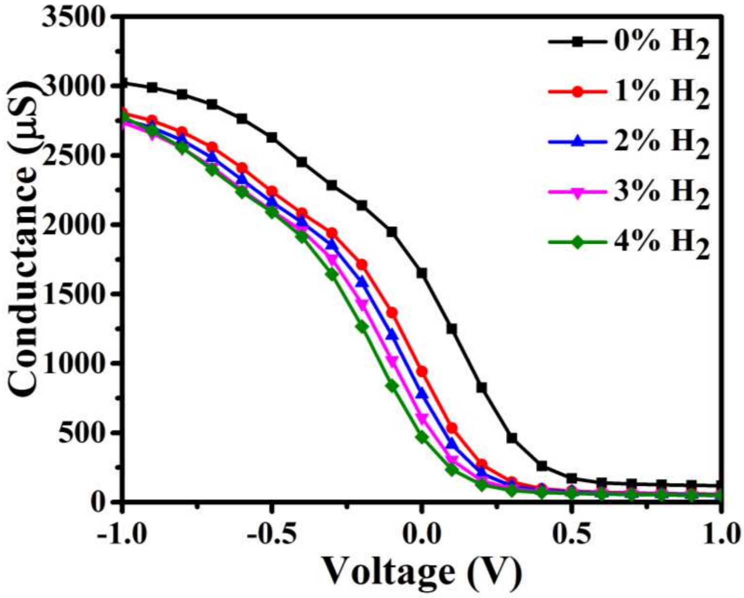

Figure 3.6: G-V characteristics at 1 MHz frequency for different concentrations of H_2.

3.3.3 Gas Sensing Characterization

When H_2 gas is exposed to the as-fabricated MOS sensor, firstly, H_2 molecules are separated on the Pd metal surface due to its catalytic behavior. Some of the H_2 atom diffuse through the Pd dot and at the TiO_2 surface these atoms polarized and made a dipole layer which is responsible for changes in the work function of Pd and this modification in work function is responsible for changes in the flat-band voltage of the fabricated device [Dwivedi *et al.* (1998), Yadav *et al.* (2007)]. There is a chemical bond between the Pd surface and chemisorbed oxygen anions on the Pd surface, which affects the work function of Pd. When H_2 is exposed on this fabricated device, a reaction between H_2 and these chemisorbed oxygen anions occurs, which is responsible for the change in the flat-band voltage (V_{FB}) of the fabricated device and a change in *C-V* characteristics occurs [Yamamoto *et al.* (1980), Yadav *et al.* (2007)]. The change in the sensor output variable provides the gas response for the sensor [Kumar *et al.* (2018)]. The gas response of the MOS sensor is calculated as the percentage change in capacitance (or conductance) defined as [Dwivedi *et al.* (1998)]:

$$\begin{aligned} Gas\ response\ (\%) &= \frac{\Delta C}{C} \times 100 \\ &= \frac{\Delta G}{G} \times 100 \end{aligned} \tag{3.1}$$

where C (G) is the initial capacitance (conductance), and ΔC (ΔG) is the change in capacitance (conductance) under gas exposer.

The capacitance characteristics have provided gas responses of 38%, 59%, 62% and 65% for 1%, 2%, 3%, and 4% of H_2 gas concentrations at 0 V, respectively. On the other hand, the conductance-based gas responses calculated at 0V are 53%, 81%, 82%, and 84% for 1%, 2%, 3%, and 4% of H_2 gas, respectively as shown in Figure 3.7.

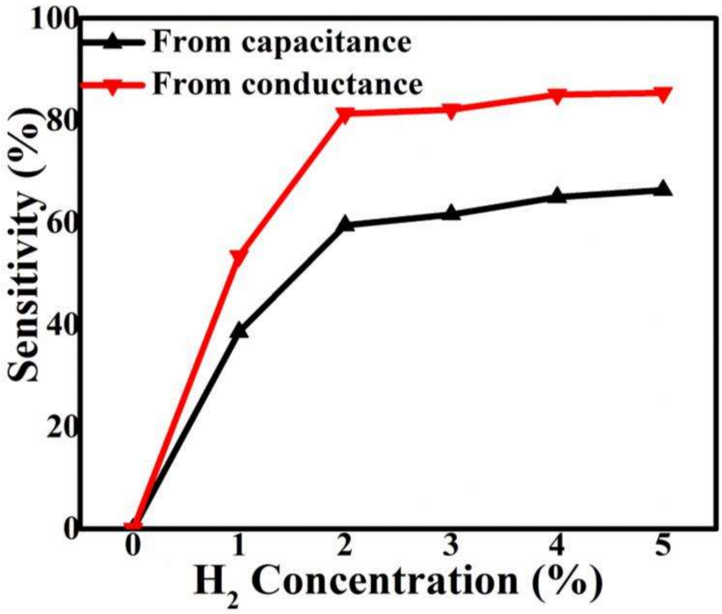

Figure 3.7: Sensitivity vs. H_2 concentration.

It is observed that gas responses based on the conductance are higher than the capacitance, and the gas response increases with increasing H_2 concentration but saturates at about 4% H_2 gas concentration. The voltage-dependent gas responses calculated using capacitance and conductance under the exposure of 4% H_2 gas are shown in Figure 3.8. The maximum gas response observed at ~0 V confirms that the as-fabricated MOS sensor can be used effectively for hydrogen gas sensing without applying supply voltage.

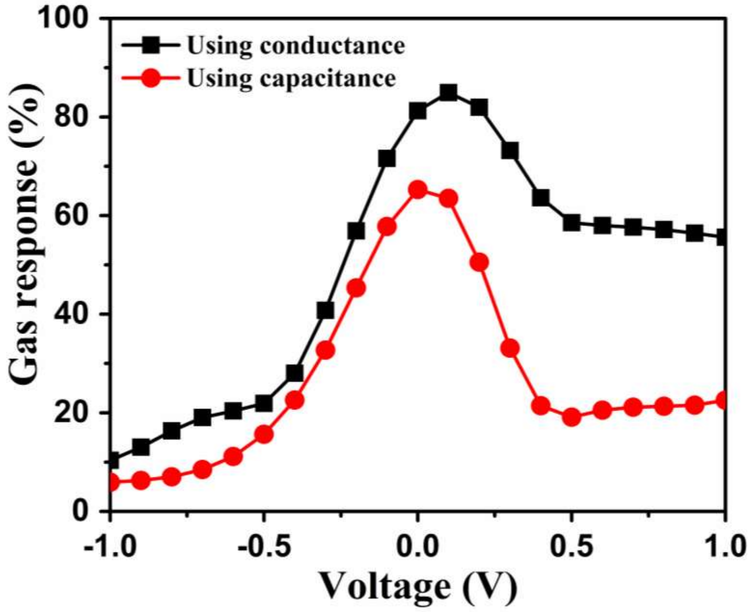

Figure 3.8: Gas response using capacitance and conductance for 4% concentration of H_2.

The flat band voltage (V_{FB}) of the as-fabricated MOS capacitor can be estimated using the following relation [Poteat *et al.* (1982), Yadava *et al*. (1990)]:

$$V_{FB} = \varphi_{ms} - \frac{Q_{SS}}{C_i} \quad (2)$$

where Q_{SS} is surface charge density, C_i is the gate-oxide capacitance and φ_{ms} is the work function difference of the metal and semiconductor of the MOS sensor. It is found that the change in conductance is more than the change in capacitance in the fabricated MOS sensor. Thus, the gas response calculated using conductance is more than capacitance. Before measuring the gas response of the fabricated sensor, we have calibrated the hydrogen concentration using commercially available gas sensors. The performance of the fabricated metal oxide-based sensor was highly accurate within ±1%. The gas response of the as-fabricated sensor is also compared with other reported Pd/TiO_2/Si-based MOS structures in Table 3.3. Our proposed sensor with 50 nm thermally evaporated TiO_2 film and porous Pd dots provides the best gas sensing results in this work.

Table 3.3: Comparison of TiO_2 based H_2 sensor.

Oxide materials	Deposition method	Working temperature (°C)	H_2 concentration (%)	Max. gas response (%)	Ref.
TiO_2	Thermal evaporation	RT	8	47	[Yadava *et al.* (1990)]
TiO_2	Thermal evaporation	RT	8	54	[Yadav *et al.* (2007)]
TiO_2	Ion-beam-sputter deposition	290	10	~96	[Joo *et al.* (2010)]
TiO_2	Thermal evaporation	RT (23)	4	84	This work

3.4 Conclusion

In this chapter, the thermally grown nanostructured TiO_2 thin film based Pd/TiO_2/Si/Al MOS sensor for hydrogen gas sensing is fabricated. The exposed hydrogen gas entered the TiO_2 thin film through the porous Pd electrode. The evaporated nanostructured TiO_2 thin film increased the gas capturing in the MOS device structure. The reduction in the capacitance and the conductance is found under the increasing exposer of hydrogen gas. The maximum shift in the capacitance and the conductance are observed around 0 V. The maximum gas response is 84% using conductance, whereas 65% using capacitance when 4% of hydrogen gas is exposed. The obtained gas response is high enough for practical application at room temperature operating conditions.