CHAPTER 2

Hydrogen Sensing Properties of Sol-Gel Derived TiO_2 Thin Film Based Interdigitated MSM Device

Contents

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2.1 Introduction

The increasing demand for energy requirements for various industrial and commercial applications are meeting by fossil fuels. However, due to the limited natural stock of fossil fuels, hydrogen gas (H_2) is projected as one of the best alternative fuels for future energy [Zhang *et al.* (2016]. H_2 is a clean energy source that can be used in a wide range of applications, such as hydrogen-powered automobiles, aerospace, power generation, and refining of metals [Dunn (2002), Liu *et al.* (2007), Benac and McAndrew (2012)]. Although H_2 is considered a clean energy source, it is very explosive and extremely flammable in the air with a lower explosive limit of 4% [Ling *et al.* (2014), Luo *et al.* (2017)]. Also, it is colorless and odorless. Therefore, the detection of any leakage of H_2 is required using an efficient and low-cost gas sensor, which must monitor the low concentration at room temperature [Wang *et al.* (2012), Haija *et al.* (2016)]. As discussed in Chapter 1, the gas sensors must have a high gas response, selective to target gas, and low response time [Balaguru and Jeyaprakash (2004), Bochenkov and Sergeev (2010)].

Both the inorganic materials (mainly metal oxides and their nanostructures) [Sberveglieri (1995), Timmer *et al.* (2005)] and organic conducting polymers [Sengupta *et al.* (2009)] have been used for fabricating the gas sensors. SnO_2 is dominantly used for the fabrication of commercially available gas sensors [Zhao *et al.* (2017)], but its poor selectivity [Timmer *et al.* (2005)], the requirement of very expensive set up [Lv *et*

al. (2017)], and poor room temperature response have greatly encouraged for the investigation of TiO_2/ZnO thin films for low-temperature based gas sensors, as discussed in Chapter-1. In view of the above, the present chapter is devoted to investigating the room-temperature hydrogen sensing capability of the sol-gel derived TiO_2 thin films. The film is used as the active material in a metal-semiconductor-metal (MSM) structure. The outline of the rest of this chapter is given as follows:

Section 2.2 presents the experimental details of the fabrication of a sol-gel derived TiO_2 thin film based MSM sensor. The results and discussion related to the film characterizations and hydrogen detections are included in section 2.3. Finally, section 2.4 has been used to conclude the objectives and outcomes of the work carried out in this chapter.

2.2 Experimental Details

2.2.1 Synthesis of Sol-gel Solution of TiO_2

The Sol-gel (SG) solution is prepared using titanium tetra isopropoxide [$Ti(OC_3H_7)_4$, ex. Ti ≥ 98 % Merck] as a starting precursor due to its better solubility in alcohols [González *et al.* (2007), Alaie *et al.* (2015)]. Initially, 12 cc of the precursor is dissolved in 170 cc of isopropyl alcohol (C_3H_8O) and after that kept the solution on a magnetic stirrer for 1 hour at room temperature [Rawat *et al.* (2015)]. As a final step, a few drops of hydrochloric acid [HCL, 2 M, 35 % Merck] are gradually added to the solution until a transparent solution is obtained. After getting the transparent solution, the solution is left for aging on the magnetic stirrer for 3 hours at room temperature. In this process, HCl is used as a catalyst to accelerate the process of hydrolysis [González *et al.* (2007)]. The SG is used for coating after further aging the solution for 24 hours and filtering it

through the PVDF membrane filter of 0.22 µm pores size from MILLEX GV. The SG solution filtering ensures that the larger size particles are filtered out from the solution. The synthesis flowchart for the sol-gel TiO_2 is shown in Figure 2.1. The synthesized TiO_2 solution under the illumination of ultraviolet light is shown in Figure 2.2.

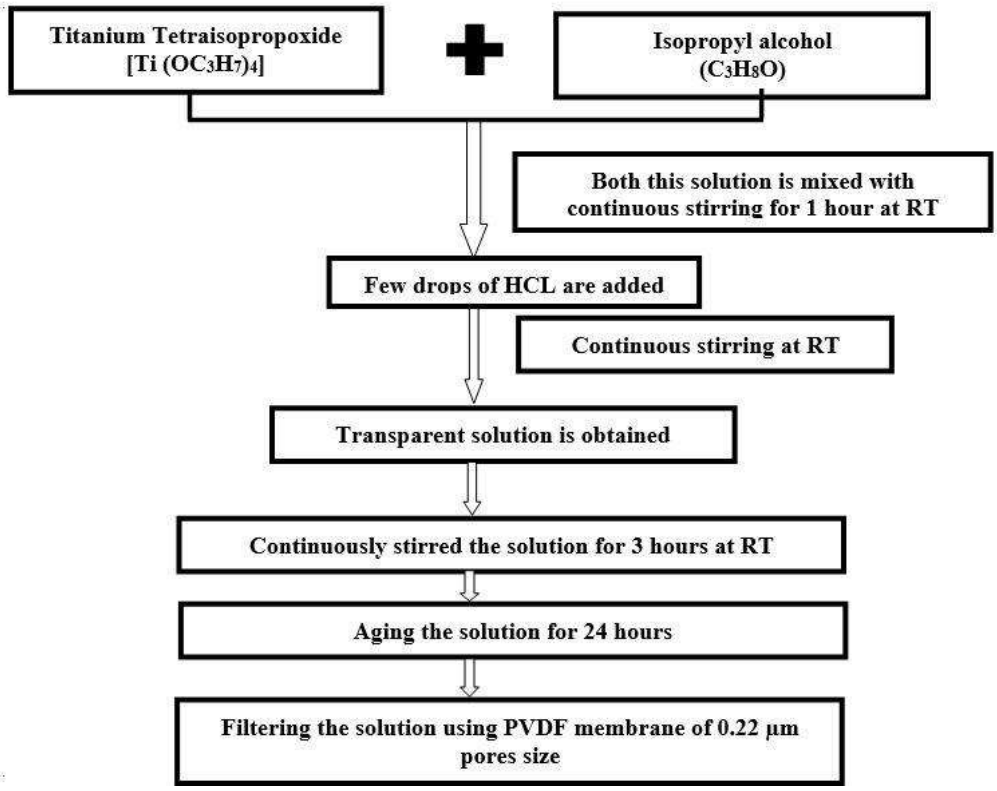

Figure 2.1: A simplified flow chart to demonstrate the Sol-gel synthesis process.

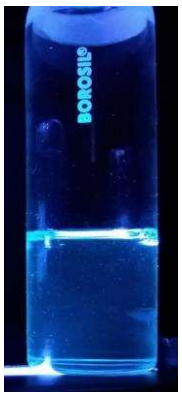

Figure 2.2: Synthesized Sol-gel solution of TiO_2.

2.2.2 Substrate Cleaning

Single-side polished and boron-doped p-type silicon (100 orientation, 2–7 Ω.cm resistivity, and 4″ diameter from Wacker-Chemitronic GmbH, Germany) in 15×15 mm^2 square size was used as a substrate in the present work. The substrates were cleaned using the standard wet chemical method in trichloroethylene, acetone, and deionized (DI) water (Resistivity 18 MΩ.cm obtained from the Millipore DI plant), ultrasonically in sequence for 10 minutes each to remove certain organic residues and contaminants. Then, the substrates were subsequently immersed in a solution of H_2SO_4 and H_2O_2 (4:6 ratio) for 30 minutes. The solution of H_2SO_4 (purity ~97 %) and H_2O_2 (purity ~30 %) was used to remove the metallic contamination from the substrates. Further, rinsed in DI water and then dipped in a solution of hydrogen fluoride (HF) and DI water (1:10 ratio) for 2 min. The immersion in HF solution was done to etch out the native silicon dioxide layer from the substrates' surface. Finally, the substrates were thoroughly rinsed in DI water and dried in a temperature-controlled oven at 110°C with the flow of nitrogen gas for 20 min. All the chemicals used were analytical grade and purchased from Merck Chemical Limited, Mumbai (India), and used without further purification.

2.2.3 Device Fabrication

After cleaning the silicon (Si) substrates, the dry oxidation process was performed in a cylindrical muffle furnace to thermally grow ~300 nm thick silicon dioxide (SiO_2) layer over the substrates. Then, the spin coating unit (TSE, Model: SPM-150LC, Germany) was used to deposit the TiO_2 layer. The prepared SG solution of TiO_2 was dropped using a micro-dropper onto the SiO_2 grown substrate placed over the substrate holder of the spin coater unit. After dropping the TiO_2 solution, the substrate was rotated at 3000 rpm for 30 sec in the spin coater. The deposited TiO_2 sol-gel film was

initially dried at 200°C for 10 minutes and finally annealed at 450°C on a hot plate for 30 minutes under ambient air conditions. The heat treatment was used to remove the organic materials and dried the TiO_2 TF surface. This post-deposition annealing treatment is used to improve the crystalline quality of the TiO_2 TFs by reducing the structural surface defects of the films [Vishwas *et al.* (2012)]. 50 nm thin film of pure Pd (99.99%) was deposited over the TiO_2 layer for forming the interdigitated MSM electrode structure with a channel length of 300 µm by a thermal evaporation method. Finally, the fabricated device was annealed at 400°C in the quartz tube of the muffle furnace (from Thermco, USA) for 7 minutes in an N_2 atmosphere. Annealing is the process of heat treatment generally used to make better contact junction [Xu *et al.* (2002), Rollett *et al.* (2004)]. It involves heat treatment at a temperature for a certain period under a suitable gas environment. After the annealing, the samples were cooled down to room temperature. The cross-sectional view of the fabricated device is shown in Figure 2.3.

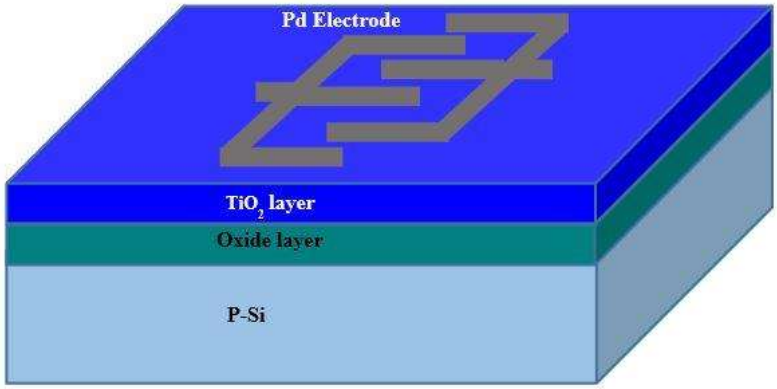

Figure 2.3: Cross-sectional view of the as-fabricated sensor.

2.3 Results and Discussion

In this section, the thin-film surface, electrical, and gas sensing characterization of sol-gel derived TiO_2 film based MSM sensor are discussed.

2.3.1 Thin Film Characterization

The thickness of the spin-coated TiO_2 film is measured as ~40 nm by an optical spectrometer commonly known as a thin film analyzer (Model No. F20-UV from Filmetrics, USA). The diffraction pattern for the spin-coated sol-gel derived TiO_2 film coated on SiO_2/p-Si substrate is obtained by the XRD (Model no. XDMAX, PC-20 18kW Cu rotating anode from RIGAKU, Japan), as shown in Figure 2.4. The analysis of the XRD results using JCPDS No. 21-1272 shows that the TiO_2 grown on the SiO_2/Si have a strong diffraction peak at $2\theta = 25.48°$ corresponding to (101) facet and others weak peaks at $2\theta = 38.75°$ corresponding to (004) facet. A very strong peak at $2\theta = 31.85°$ is corresponding to Si substrate. XRD analysis indicates that TiO_2 is of high quality and phase purity with good crystallinity.

The sol-gel derived TiO_2 film roughness is calculated from AFM image (scanning probe microscopy, Model No. NTEGRA Prima from NT-MDT Services and Logistics Ltd., Ireland) in Figure 2.5. The roughness parameters such as average roughness, root mean square (RMS) roughness, and peak to peak spacing for the sol-gel derived TiO_2 film using Nova PX software are shown in Table 2.1. These parameters confirm that the film has nano-level roughness, which is suitable for fast recovery and better sensor performance [Pandey *et al.* (2014)].

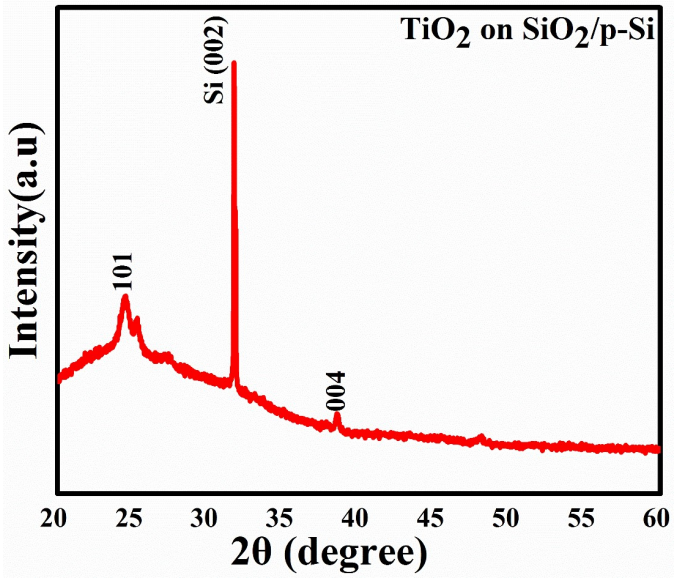

Figure 2.4: XRD image of the TiO_2 thin film on SiO_2/p-Si substrate.

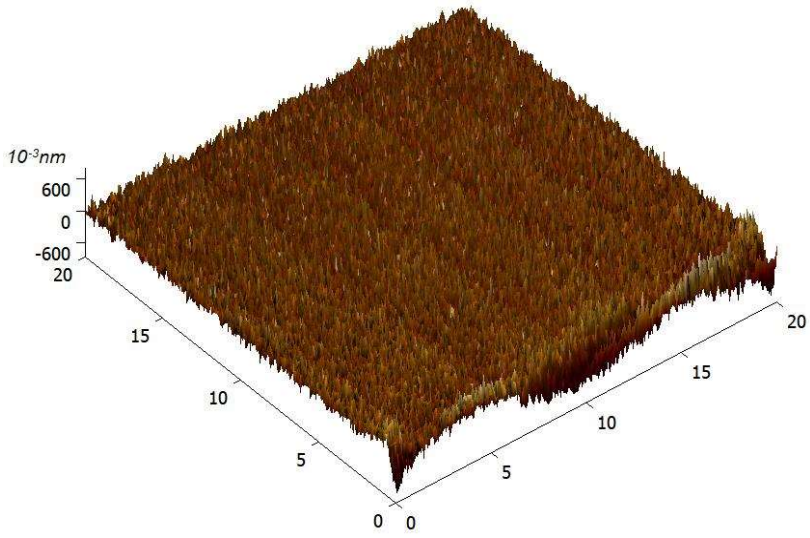

Figure 2.5: AFM image of the TiO_2 thin film annealed at 450°C.

Table 2.1: Surface parameters for Sol-Gel derived TiO_2 films.

Parameters/Film	Sol-Gel derived TiO_2
Average roughness (nm)	0.1
RMS roughness (nm)	0.2
Peak to peak spacing (nm)	1.6

The sol-gel derived TiO_2 film's surface morphology is studied using SEM images (SEM, Model: EVO MA 15/18, from Carl Zeiss Microscopy Ltd., UK), as shown in Figure 2.6. The SEM image of the sol-gel derived TiO_2 film on SiO_2/ p-Si substrate indicates that the grown film is of high purity and uniformity.

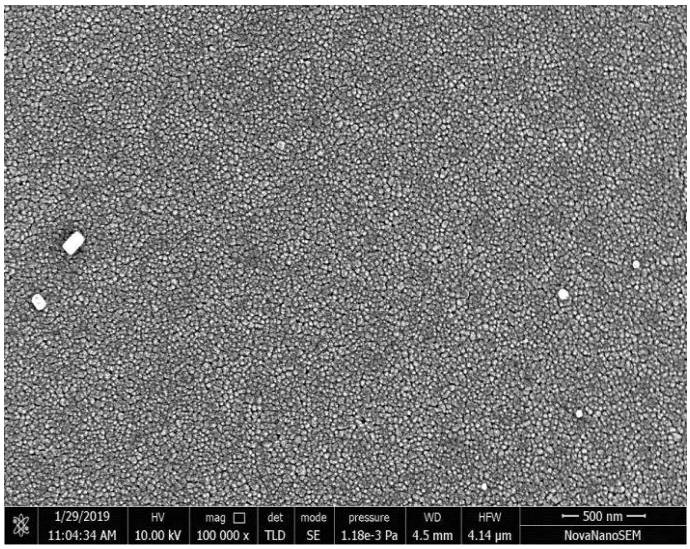

Figure 2.6: SEM image of sol-gel derived TiO_2 thin film on SiO_2/ p-Si substrate annealed at 450°C.

The fabricated device's elemental composition is estimated from the EDS image (EDS from Oxford, UK), as shown in Figure 2.7. The peaks corresponding to the energy of the elemental compositions of titanium, silicon, palladium, and oxygen were present. Smaller peaks for titanium, palladium, and oxygen than Si are due to TiO_2 and Pd's thinner layer than the SiO_2/Si. The weight percentages of Ti, Pd, Si, and oxygen are ~1.92 %, 25.24 %, 67.47 %, and 5.38 %, respectively while their respective atomic percentages are ~1.33 %, 7.87 %, 79.66 %, and 11.15 %, respectively. The respective weight % and atomic % for each element present are also mentioned in Table 2.2.

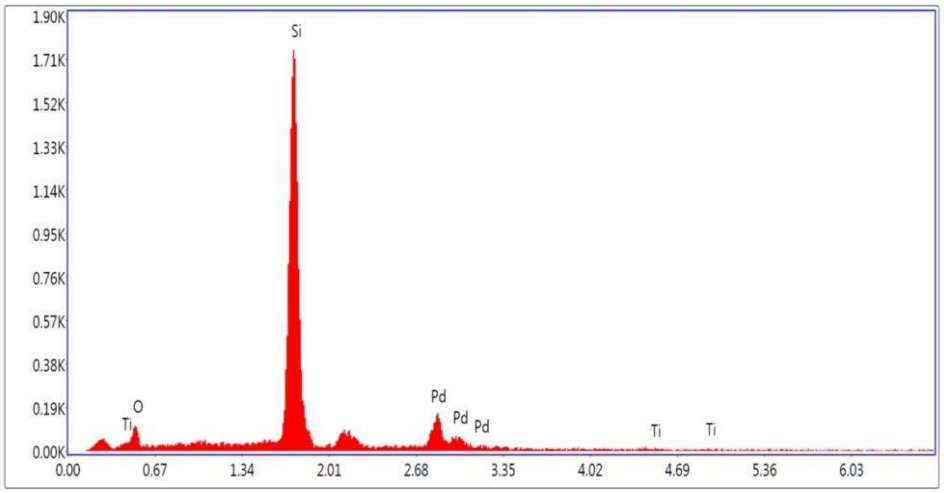

Figure 2.7: EDS image of sol-gel derived TiO_2 thin film on SiO_2/ p-Si substrate.

Table 2.2: Details of respective elements present in the fabricated device.

Elements	Weight (%)	Atomic (%)
Ti K	1.92	1.33
Pd L	25.24	7.87
Si K	67.47	79.66
O K	5.38	11.15

2.3.2 Electrical and Gas Sensing Characterization

The fabricated device is placed in a homemade gas sensing setup (already discussed in Chapter 1) for electrical characterization. The current-voltage (*I-V*) characteristics of the sol-gel derived TiO_2 thin film based interdigitated MSM sensor under the ambient condition without exposure of hydrogen gas at room temperature have been shown in Figure 2.8. The perfect linear *I-V* characteristic is obtained due to the formation of ohmic contact between TiO_2 thin film and Pd electrode. The specific amount of analyte gases in pure form are injected inside the gas chamber using an attached mass flow controller (MFC, model MC-100 SCCM from Alicat Scientific Inc., USA) at the inlet of the gas chamber. It is found that there is no change in the *I-V* curve for 1% hydrogen

gas at room temperature, as shown in Figure 2.8. In other words, the sol-gel derived TiO_2 thin films are found to be non-suitable for room-temperature hydrogen sensing applications.

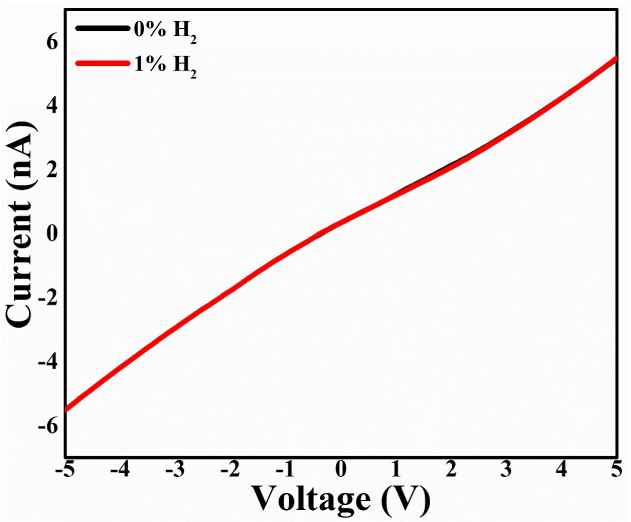

Figure 2.8: *IV* characteristic of the fabricated sensor for 0% and 1% hydrogen gas under the ambient condition at room temperature.

The *I-V* characteristics at different temperatures without hydrogen exposure and the *I-V* characteristics at different temperatures with 1% of hydrogen exposure are shown in Figure 2.9 and Figure 2.10, respectively. No change in current at room temperature and 100ºC is observed for 1 % hydrogen, whereas a small change in current is observed at 150ºC. A significant change in current is observed at 175ºC for 1% hydrogen gas exposure.

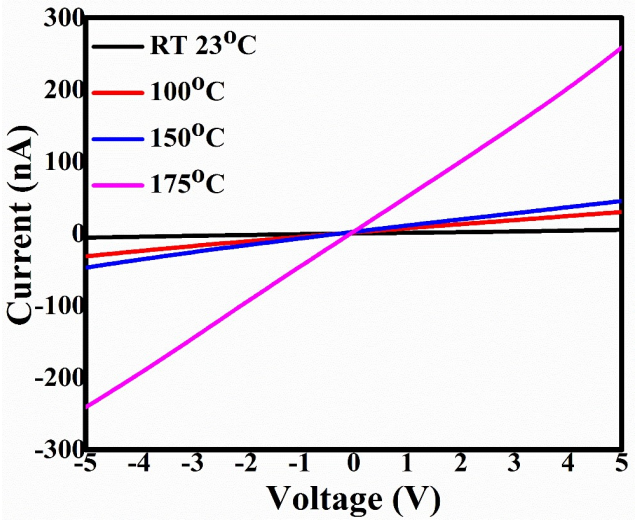

Figure 2.9: *IV* characteristic at different temperatures without hydrogen exposure condition.

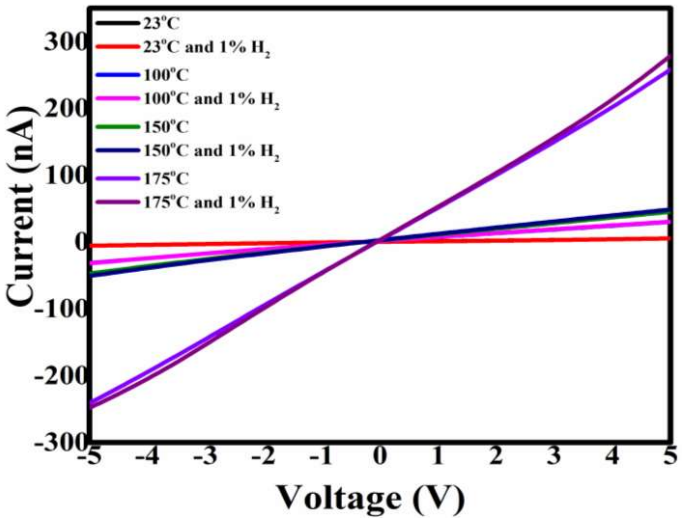

Figure 2.10: *IV* characteristic at different temperatures underexposure of 1% H_2 gas.

The *IV* characteristics at 175°C under the exposure of different H_2 gas concentrations are shown in Figure 2.11. It is found that the sensor current increases with hydrogen concentration. The measurements are limited to the maximum temperature of 175°C due to the higher temperature limitation of the gas sensing setup. On the semiconductor's surface, the phenomena of adsorption and desorption appear very rapidly, which results in a significant change in the electrical conductivity of TiO_2

thin film. O_2^{-1} is the principal species for the chemisorption of oxygen at lower or room temperature, whereas, at the higher temperature, chemisorbed O_2^{-1} donates an electron to TiO_2 ($O_2^{-1} \rightarrow O_2 + e$); hence conductivity increases [Chang (1980)].

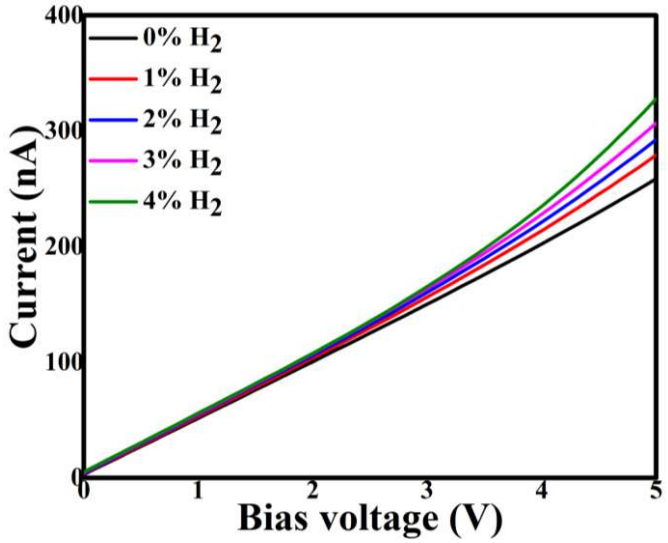

Figure 2.11: *IV* characteristic at different H_2 concentrations and fixed temperature of 175°C.

When the proposed sensor is exposed to H_2 gas at higher temperatures, the H_2 molecules first react with the remaining adsorbed oxygen ion on the sensor surface and then with the TiO_2 surface. At the surface of the sensor, multiple chemical reactions happen [Ren *et al*. (2011)], and electrons are released to the conduction band of TiO_2, which decreased the resistance of film and increased the current.

$$\begin{aligned} 4H + O_2^- &\rightarrow 2H_2O + e^- \\ 2H + O^- &\rightarrow H_2O + e^- \\ 2H + O^{2-} &\rightarrow H_2O + 2e^- \end{aligned} \tag{2.1}$$

The sensor performance parameter, gas response (S), is defined as [Mondal *et al*. (2014)]:

$$Gas\ response(S) = \frac{I_{H_2} - I_{air}}{I_{air}} \times 100\% \tag{2.2}$$

where I_{air} and I_{H_2} are the currents measured under ambient air and different H_2 concentrations, respectively. The gas responses are 7.93%, 13.14%, 18.62%, and 26.75% for 1% H_2, 2% H_2, 3% H_2 and 4% H_2 gas, respectively at 5 V of applied voltage. The gas responses significantly depend on the applied bias voltage, as shown in Figure 2.12.

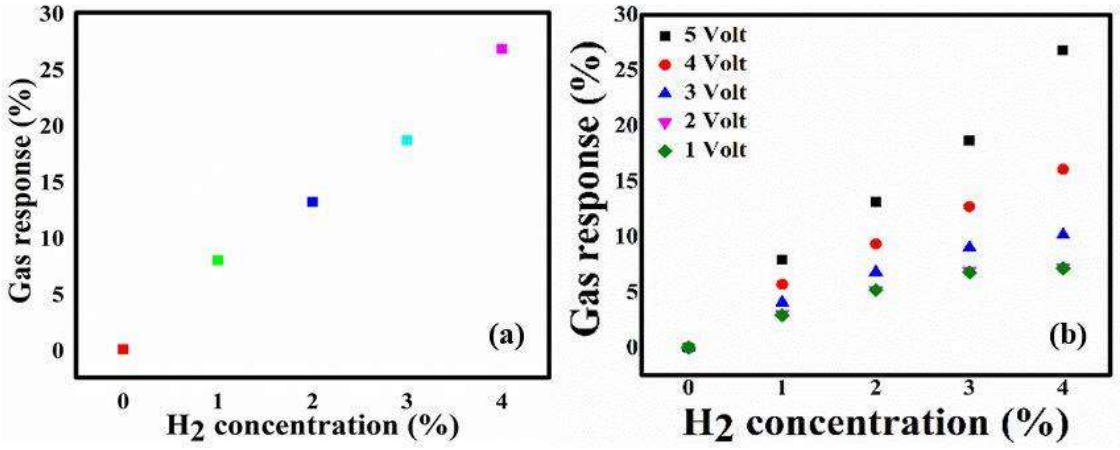

Figure 2.12: (a) Gas response vs. H_2 concentration plot at a bias voltage of 5 V and temperature of 175°C and (b) gas response vs. H_2 concentration plot at different voltages and fixed temperature of 175°C.

2.4 Conclusion

In this chapter, a TiO_2 thin film based interdigitated MSM sensor for H_2 gas sensing is fabricated. The Sol-Gel technique is used to prepare the TiO_2 solution, and the solution is deposited on the Si/SiO_2 substrate by the spin coating technique. The EDS measurement is used to estimate Ti and oxygen, whereas SEM and AFM analyses are used to find the surface morphology of the TiO_2 thin film. After exposure to H_2 gas, a significant shift in *I-V* characteristics is observed at the higher temperature (175°C), whereas no change in *I-V* characteristics is observed at room temperature. The proposed MSM sensor shows a negligible hydrogen response at room temperature, but the

maximum response of 26.75% at 175°C for 4% hydrogen. The proposed sensor's hydrogen response is dependent on the applied bias voltage, and the maximum response is observed for the 5 V bias voltage. The obtained H_2 gas response is based on the change in the conductivity of sol-gel derived TiO_2 thin film in the MSM device structure.