CHAPTER 8

Tungsten Oxide Based Hydrogen and Methane Gas Sensors
This chapter deals with the $H_2$ and Methane gas sensing studies of a few tungsten oxide based nanostructured thin films prepared by pulsed laser deposition technique. Among the investigated samples, Pd incorporated tungsten oxide films present promising $H_2$ sensing and selective response to $H_2$ gas at relatively lower operating temperatures.
8.1 Introduction

The demand for a hydrogen sensor with high sensitivity, fast regeneration, and an even faster response time is gaining momentum as efforts to develop a hydrogen economy continue to grow [1,2]. Hydrogen has a much wider range of flammability in air (4% to 75% by volume) and the lowest limit of hydrogen concentration in air to explosion is 4.65% [3]. These characteristics indicate that flammability is a greater risk for hydrogen than for other fuels. Methane is the major constituent of natural gas, the major poisonous pollutant of incomplete combustion of hydrocarbon fuels and ethanol, and has a significant greenhouse effect. Unmonitored methane can accumulate, and can cause dangerous explosions. So, the development of a hydrogen and methane sensor with high performance, able to detect from ppm level to a few percentage of the gas in air is very much imperative.

Tungsten oxide is a widely studied material for the development of solid-state devices based on thin and thick films. The most successful results have been obtained on electrochromics and gas sensor fields. Focusing on gas sensors, most of the work has been devoted to conductometric devices due to their small size, low cost, low power consumption and high compatibility with electronic signal processing. WO$_3$ thin films have remarkable gas sensing properties that account for the considerable attention they have been given for the past few years. WO$_3$ has proved to be highly sensitive even to very low concentrations of NO$_x$ [4], H$_2$S [5], NH$_3$ [6] or CO [7]. The response of WO$_3$ to these gases is at least as good as that of SnO$_2$, the binary metal oxide that has received by far the most attention up to now among sensor materials. Moreover, WO$_3$ is considered as one of the best candidates for NO$_x$ sensing due to its good selectivity to low concentrations of NO$_x$ gas [8]. Being a wide band gap n-type semiconductor, the sensing mechanism of the WO$_3$ sensor is based on the change of film resistance due to physisorption, chemisorption and catalytic reactions of gas-phase species with the film surface. Recent reports show that, WO$_3$ thin films doped by noble metals like Pd, Pt and Au are more sensitive, selective and highly responsive to NO$_x$ gas.
There are only a few reports on the tungsten oxide based hydrogen and methane gas sensors. Hoel et al., [9] studied the H$_2$ sensing properties of WO$_3$ and Pd:WO$_3$ films and reported a sensitivity of ~ 100 and 6 respectively for the Pd:WO$_3$ film heat treated at 773 K and 873 K towards 500 ppm of H$_2$. Lee et al. [10] reported the Raman spectroscopic studies of gasochromic a-WO$_3$ and Pd: a-WO$_3$ films towards hydrogen gas. Investigations of thin film structures of WO$_3$ and WO$_3$ with Pd for hydrogen detection in a surface acoustic wave (SAW) sensor system was reported by Jakubik [11]. The response and recovery times of the reported bilayer structure in the SAW system was very short (~100-150 s for the response – depending on the hydrogen concentration and ~100 s for its recovery) which is very important from the practical point of view. The present chapter discusses the H$_2$ and CH$_4$ gas sensing properties of tungsten oxide films incorporated with Pd, titania and nitrogen prepared by pulsed laser deposition technique. Pd and Pt are considered as catalytic dopants. Catalytic additives increase the rate of specific reactions on the surface of WO$_3$ grains due to spill-over effect or modification of surface energy states.

8.2 Experimental Details

For the gas sensing studies, laser ablated tungsten oxide films incorporated with Pd, TiO$_2$ and nitrogen, deposited on quartz substrate are selected. For hydrogen gas sensing studies tungsten oxide films incorporated with 5 wt % Pd, [deposited at $pO_2 = 0.12$ mbar and $T_s = 873$ K], 10 wt % TiO$_2$ [deposited at $pO_2 = 0.12$ mbar and $T_s = 873$ K] and nitrogen incorporated films [deposited at $pN_2 = 0.17$ mbar and $T_s = 973$ K] are used. For methane sensing, tungsten oxide film incorporated with 5 wt % Pd, [deposited at $pO_2 = 0.12$ mbar and $T_s = 873$ K] is only used. The preparation and characterization of these films are discussed in previous chapters.

Platinum dots of 0.5 mm diameter (100 nm thick, 1 mm edge to edge spacing) are sputter coated onto these films and are then mounted on sample holders. For electrical contacts, gold wires (1 mm -diameter) are bonded onto the platinum dots using a Mech-El-907 Ultrasonic wire bonder (Mech-El Industries, Massachusetts, USA). The mounted samples are kept inside a tube furnace equipped with a digital temperature controller, and
the external electrical connections are taken through metal pins connected with the furnace. A laminar flow of test gases through the furnace is maintained and managed by a computer controlled mass flow controller (MKS Instruments, Texas, USA) and the resistance variation in samples at different temperatures and for a specific concentration of gas are recorded by a computer interfaced Keithley 6517A Electrometer/High resistance meter. The volume of the cylindrical chamber used for the sensing studies is around 300 cm$^3$. Resistive heating mechanism is used for sample heating. The temperature of the heater (temperature ramp rates and dwells) is controlled by a microprocessor based temperature controller, a solid state relay and a chromel-alumel thermocouple (for feedback).

Dry oxygen gas is used throughout the experiments as the reference gas for the gas sensing measurements in order to simplify the experimental set up. The baseline will not shift significantly even if it is dry air. Humidity inside the sensing chamber is maintained less than 2% and for all practical purposes it can be considered 'dry'. It is known that humidity can increase the sensitivity of the gas sensor to reducing gases. Hence the measured gas response values in dry air will be lower than that in real working conditions, where water vapour is present. If humid air is introduced inside the system, several precautions are to be taken to avoid condensation at ambient temperature. A strict control of gas temperature and pressure has then to be ensured inside the system that makes the experimental set up complex. In the present investigation, oxygen gas is used for baseline stabilization. Due to safety reasons and the difficulty in maintaining low flow rate, the gases to be sensed (H$_2$ and CH$_4$) are admitted as a mixture of 1% of the respective gas in nitrogen. Preliminary gas sensing studies of the samples are performed at 323 K for hydrogen gas. The hydrogen gas sensing studies of the 5 wt % Pd incorporated WO$_3$ are done at temperatures 373, 423 and 473 K. Sensing studies of 5 wt % Pd incorporated WO$_3$ films to methane gas are done at 423 and 473 K.

The samples are heated in dry oxygen gas to the set temperatures while monitoring the resistance and are allowed to stabilize at the chosen temperatures. The saturation process itself takes a particular time depending on the sample and operating
temperature. Then the samples are exposed to a pre-determined concentration of test gas and the change in resistance is monitored. At the saturation point of the adsorption, the gas flow is stopped and the experiment chamber is evacuated of test gas and the oxygen gas is re-entered. Then the resistance value is allowed to recover its original value and this process is repeated in cycles.

8.3 Results and Discussion

8.3(a) H$_2$ Gas Sensing Studies at Different Operating Temperatures

Figure 8.1(a) & (b) depict the change in resistance after the introduction of the H$_2$ gas [1% H$_2$ in N$_2$] for the nitrogen incorporated WO$_3$ film (abbreviated as NW) and titania incorporated WO$_3$ film (abbreviated as TW) respectively at an operating temperature of 323 K. The film resistance is found to decrease rapidly, from 3.29 MΩ to 1.81 MΩ for NW films and 27.83 MΩ to 15.04 MΩ for TW films respectively on introduction of the H$_2$ which is the expected response of an n-type metal oxide semiconductor towards a reducing gas. The response times obtained for NW and TW films are 1.33 and 7 minutes respectively. The recovery time (the time taken to achieve 90% of the initial resistance on removal of the test gas) is found to be very high at this temperature for both films and is not measured due to its poor recovery feature as evident from Figure 8.1.

![Figure 8.1](image_url) Response curve of (a) N:WO$_3$ and (b) TiO$_2$: WO$_3$ films towards 1% H$_2$ in N$_2$ at an operating temperature of 323 K
The measured DC electrical resistance values for both the film sensors are subsequently used to obtain the gas sensitivity of the sensors using the relation [12],

$$S = \frac{(R_0 - R_s)}{R_s}$$  \hspace{1cm} 8.1

where $R_0$ is the base line resistance/ resistance in dry oxygen and $R_s$ is the saturation resistance / final resistance in H$_2$ gas. For the NW and TW sensors at an operating temperature of 323 K, relatively low sensitivity values of 0.816 and 0.8493 respectively are obtained [Table 8.1].

![Graph](image)

**Figure 8.2** Dynamic response curve of Pd:WO$_3$ film towards 1% H$_2$ in N$_2$ at an operating temperature of 323 K

Figure 8.2 shows the transient response of the Pd incorporated WO$_3$ film (abbreviated as PW) sensor towards hydrogen gas [1% H$_2$ in N$_2$] at an operating temperature of 323 K. Compared to NW and TW sensors, the PW sensor exhibits relatively high response time ~ 37 minutes and low recovery time of ~ 56 minutes. Also this sensor exhibits a fairly higher sensitivity of 4 at this temperature. Though the PW film sensor exhibits reasonably higher response time, compared to NW and TW sensors, it possesses better sensitivity and recovery features. Hence this sensor is only taken for optimization of H$_2$ gas sensing studies.
Figure 8.3 Dynamic response curve of Pd:WO$_3$ film towards 1% H$_2$ in N$_2$ at an operating temperature of 373 K

Figures 8.3-8.5 show the transient sensing plots (dynamic response curve) of PW sensor for H$_2$ gas at operating temperatures 373, 423 and 473 K respectively. The sensor parameters obtained are listed in Table 8.1. From the transient response curves Figures 8.2-8.5] it is obvious that, the resistance almost reaches its initial value after the test gas has been shut off and it proves that the adsorption process is infinitely reversible. It can be seen that both the response time and recovery time decreases with increase in operating temperature [Figure 8.6]. Response time is defined as the time required for the resistance to undergo a 90 % variation with respect to its equilibrium value following the introduction of a particular concentration of test gas into the test chamber. Like wise, recovery time is defined as the time required for the resistance to return to 10% below its equilibrium value in air following letting out the test gas and introducing the reference gas. In the present case, to get a comparison on recovery time of PW sensor towards H$_2$ gas at various operating temperatures we have estimated the time required for the resistance to return to 30 % below its equilibrium value in reference gas. At low temperatures, the reaction between the oxygen species [O$^-$ and O$_2$$^-$] adsorbed on the sensor and the H$_2$ gas occur slowly and takes a long time for H$_2$ gas to be consumed resulting in longer response and longer recovery time. At high temperatures, the rapid
reaction of adsorbed oxygen species with the H\textsubscript{2} gas and the enhanced mobility of H\textsubscript{2} molecules on the sensor surface can account for the observed decrease in response time and recovery time at higher temperatures.

![Graph showing transient response of Pd: WO\textsubscript{3} film towards 1% H\textsubscript{2} in N\textsubscript{2} at an operating temperature of 150°C.](image)

**Figure 8.4** Transient response of Pd: WO\textsubscript{3} film towards 1% H\textsubscript{2} in N\textsubscript{2} at an operating temperature of 423 K

The sensitivity of the sensor is found to increase with increase in operating temperature up to 423 K and decreases thereafter [Figure 8.7]. The highest value of
sensitivity ~ 777 is obtained at 423 K for the PW sensor. For a particular pair of sensing material and test gas, there is an optimum temperature range for best sensing operation. In the present investigation, it is found that for H\textsubscript{2} gas sensing, PW sensor has the optimum temperature ~ 423 K for the best sensing operation. The kinetics of gas detection is determined by oxygen adsorption/desorption (A/D) processes [13]. As the operating temperature increases, the surface diffusion of adsorbed oxygen species and the adsorption rate of H\textsubscript{2} gas on the device active layer get enhanced, generating more charge carriers resulting in higher sensitivity [14]. Further increase in operating temperature of the sensor can change the equilibrium of the adsorption/desorption reaction with H\textsubscript{2} gas. The decrease in the number of active adsorption sites when the temperature of the sensor is raised causes a reduction of the sensor response to H\textsubscript{2} at working temperatures higher than 423 K. Lewis et al. have reported that decrease in the solubility of hydrogen in palladium at relatively high temperature can also contribute to the decrease in sensitivity beyond 423 K [15].

![Figure 8.6 Variation of response time and recovery time as a function of operating temperature](image.png)
Shimizu et al. reported the H$_2$ sensing characteristics of Pt/WO$_3$ films towards 0.8 % H$_2$ in dry base gas mixture (O$_2$/N$_2$) and reported a sensor repose of ~ 99 at 573 K [16]. Optical hydrogen sensing of Pd-WO$_3$, Pt-WO$_3$ and Au-WO$_3$ composite films towards 1 vol. % of H$_2$ in air at a temperature range 473- 523 K is reported by Ando et al. [17]. Incorporation of Pd in WO$_3$ is found to enhance the H$_2$ detection in air through an increasing change of absorbance in the whole visible – near IR wavelength region centered at $\lambda = 1000$ nm by the formation of H$_x$WO$_3$ [17]. Kandasamy et al. fabricated and demonstrated the H$_2$ and propene gas sensing properties of Pt/WO$_3$/SiC devices towards 0.125 – 1 % test gases operating in the temperature range 803 – 923 K. They reported low hydrogen sensitivity for the investigated active layer. The response time and recovery time are respectively 85 and 125 s. [18]. Fabrication and calibration of a H$_2$ sensor based on chemically vapor deposited Au-activated WO$_3$ films on silicon substrates is reported by Davazoglou et al. Devices are found to be sensitive to concentration of H$_2$ down to 100 ppm. The maximum sensitivity of approximately 50 % is observed at temperature around 393 K to 1000 ppm of H$_2$ [19]. Hydrogen sensing characterization of an electrodeposited WO$_3$ thin film gasochromic sensor activated by Pt is reported by Hsu et al.. Sensor properties of the WO$_3$/Pt films are investigated at room temperature in H$_2$-$
N₂ gas mixture containing 1-50 mol % of H₂. The transmittance change (ΔT) of the electrodeposited WO₃ hydrogen sensor is found to be ~2% when the concentration of H₂ is 5 mol % and ~20% when the concentration of H₂ is 50 mol %. The response time and recovery time are in the range of 5-60 s respectively [20]. Davazoglu et al. have reported H₂ sensing studies of Au-WO₃ films for 200-5000 ppm H₂ concentration at an operating temperature of 523-623 K with response time less than 1 minute [21].

In the present study, the very high sensitivity of PW sensor to H₂ gas at a relatively low operating temperature such as 423 K with very low response time and recovery time are significant from the device fabrication point of view. Most of the reported WO₃ based and SnO₂ based H₂ gas sensors operate at a temperature between 573 and 673 K [22, 23]. High operating temperature of the sensor makes the system complex and expensive and increases the power consumption. Pd incorporated nanostructured WO₃ films in the present study is proved to be very effective in fabricating H₂ sensor devices working efficiently at lower operating temperatures such as 423 K with higher response to H₂ gas. In the present investigation the active sensor layer is deposited on quartz substrates and better sensor performance can be expected if the active layers are fabricated on Si wafer and Al₂O₃ substrates.

8.3(a).i. Kinetics of H₂ Gas Response

The kinetics of the response to H₂ gas by Pd: WO₃ is a complex process involving the superposition of two phenomena, one occurring on the bare WO₃ oxide surface and the other on the metallic clusters. The interaction of such a surface with reducing gas involve a more complicated mechanism involving removal of lattice oxygen, modification of tungsten oxidation state and creation of new bonds between native and dopant metals. It is well known that, the adsorbed oxygen on the surface of n-type semiconductors in the equilibrium state can be observed in different forms: O₂, O₂⁻, O⁻, O²⁻ [24]. The ionization state of the oxygen adsorbed depends on the temperature, and at temperatures above 423 K, the atomic species dominate. These adsorbed oxygen species plays a crucial role in the sensing properties of the sensor materials, depending on the operating temperature [25].
The H₂ gas sensing of PW sensor can be explained by the chemical dissociation of O₂ molecules to more active oxygen ions (spillover effect) or by electron activation [26, 27] on the active sensing layer. The phenomenon of oxygen spill over can be defined as the migration of adsorbed chemical species from the metal catalyst particles onto the oxide support. It is well known that oxygen can dissociatively adsorb on the palladium surface even at room temperature as shown in relation 8.2.

\[ O(Pd) + \delta e^- \rightarrow O^{\delta-}(ad) \quad \delta = 1,2 \]  \hspace{1cm} 8.2

Thus oxygen spill over from Pd to the WO₃ surface can become an important source of active atomic oxygen for H₂ catalytic reaction on the WO₃ film surface. Oxide species can also be produced on the oxide surface as shown in relation 8.3.

\[ \frac{1}{2}O_2 + \delta e^- \rightarrow O^{\delta-}(ad) \quad \delta = 1,2 \]  \hspace{1cm} 8.3

Here \( O^{\delta-}(ad) \) is a charged oxygen species adsorbed on the oxide surface. Then the basic reaction scheme between the adsorbed oxygen species on the WO₃ surface and molecular H₂ (the test gas) gas can be expressed in a single step process as shown in relation 8.4 [28],

\[ H_2(g) + O_{ad}^-(WO_3) \rightarrow H_2O(g) + (WO_3) + e^- \]  \hspace{1cm} 8.4

H₂ gas can also dissociatively adsorb on the Pd and the additional reaction schemes can be written as [28]

\[ H_2(g) \rightarrow H + H \text{ (dissociation)} \]  \hspace{1cm} 8.5

\[ H + WO_3 \rightarrow H_{ad}(WO_3) \]  \hspace{1cm} 8.6

\[ H_{ad}(WO_3) + O_{ad}^-(WO_3) \rightarrow OH_{ad}^-(WO_3) \]  \hspace{1cm} 8.7

\[ OH_{ad}^-(WO_3) + H_{ad}(WO_3) \rightarrow H_2O(g) + (WO_3) + e^- \]  \hspace{1cm} 8.8
In either reaction path, $H_2O(g)$ is liberated as the final reaction product, resulting in accumulation of electrons at the surface which is responsible for the increase of conductance and hence the better sensitivity for PW sensor for H$_2$ gas.

Srivastava et al., [29] have reported that Pd can respond towards gases through electronic sensitization mechanism also. According to this mechanism, Pd forms Pd(II)O which then get reduced in the presence of reducing gases like H$_2$ thereby decreasing the resistivity. It is difficult to unambiguously identify which mechanism is dominating in the H$_2$ gas sensing in the present investigation and we presume both mechanism can have its own contribution in enhancing the H$_2$ gas sensing property of PW sensor. In chapter 6 under section 6.3 (e), in the micro-Raman spectrum of 5wt % Pd incorporated WO$_3$ films, a shoulder at 637 cm$^{-1}$ is observed which can be have contribution from B$_{1g}$ mode of PdO. This gives an indication that the formation of PdO in the PW films used for sensing operation and suggests that electronic sensitization of Pd can also have a contribution for the better sensing mechanism of the PW sensor for H$_2$ sensing.

8.3(b) Methane Sensing Studies

In several situations it is essential to be able to measure the composition of a gas mixture, discriminate between or quantify different gas mixtures (odors), or in some cases to give a 'fingerprint', which represents the gas mixture. A property of crucial importance of a gas sensor system is the ability to identify/quantify attributes of the examined analytes. This property is referred to as the selectivity of the gas sensor system. Most of the metal oxide sensors respond to a number of gases and hence it is difficult to explicitly identify whether the change in the measurand [in the present case the resistance] is induced by the particular test gas or not. This limits the wide application of metal oxide semiconductor gas sensors. In the present case, PW sensor presents an excellent sensing performance towards H$_2$ gas with high sensitivity at relatively lower operating temperature. In order to check the cross-sensitivity of the PW sensor to other gases, sensing studies is performed for 1% CH$_4$ methane gas under identical experimental conditions. Methane is selected as it is a light reducing gas which is highly inflammable.
Figure 8.8 Transient response of Pd:WO₃ film towards 1% CH₄ in N₂ at an operating temperature of 423 K

Figure 8.9 Transient response of Pd:WO₃ film towards 1% CH₄ in N₂ at an operating temperature of 473 K

Sensing studies to methane gas are done at 423 and 473 K under which better sensing performance is obtained for H₂ gas. Figure 8.8 and 8.9 show the methane gas...
sensing properties of PW sensor at operating temperatures 423 and 473 K. The sensitivity, response time and recovery time calculated for the PW sensor towards 1 % CH4 in N2 is listed in Table 8.1. Even though the response time and recovery time for CH4 gas sensing is lower compared to H2 sensing under these operating temperatures, the sensitivity of the PW sensor towards CH4 gas is very less, implying the better selective response of PW sensor to H2 gas.

8.3 (b).i. Methane Sensing Mechanism

Methane is a hydrocarbon and methane sensing by Pd: WO3 involves the adsorbed oxygen such as $O^-$, $O^{2-}$, $O_2^-$ on the oxide film surface as given by relations 8.2 and 8.3. The reaction 8.9 and 8.10 then follows the 8.2 and 8.3. Methane, the hydrocarbon (HC) first get adsorbed on the oxide to give the $HC(ad)$ species which react with $O^{\delta-}(ad)$,

$$HC(ad) + O^{\delta-}(ad) \rightarrow HC:O(ad) + \delta e^- \quad 8.9$$

$$HC:O(ad) + O^{\delta-}(ad) \rightarrow CO_2 + H_2O + \delta e^- \quad 8.10$$

Electronic sensitization of Pd can also have a contribution for the sensing studies of PW sensor. Dissociative adsorption of CH4 on Pd is not possible as for H2 and this can be the reason for the decreased sensitivity of the PW Sensor towards CH4 gas compared to H2 gas.

8.4 Conclusion

Hydrogen gas sensing properties of nitrogen, titania and Pd incorporated WO3 films at an operating temperature of 323 K is studied. The H2 gas sensing properties of Pd: WO3 films as a function of operating temperatures yielded high sensitivity of ~777 at low operating temperature of 423 K. The very low sensitivity of this film towards methane gas under identical experimental conditions, obviously suggests the selective response of this film towards H2 gas at this operating temperature.
### Table 8.1 Hydrogen and Methane sensor characteristics of N: WO₃, TiO₂: WO₃ and Pd: WO₃ as a function of operating temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test Gas</th>
<th>Operating temperature (K)</th>
<th>Response time (min.)</th>
<th>Sensitivity</th>
<th>Recovery time (min.)</th>
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<tbody>
<tr>
<td>N: WO₃</td>
<td></td>
<td>323</td>
<td>1.33</td>
<td>0.816</td>
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<tr>
<td>TiO₂: WO₃</td>
<td></td>
<td>323</td>
<td>7</td>
<td>0.849</td>
<td></td>
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<tr>
<td></td>
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<td>4</td>
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<td></td>
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<td>777</td>
<td>112</td>
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<td></td>
<td></td>
<td>473</td>
<td>0.87</td>
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<td>10</td>
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<tr>
<td>Pd: WO₃</td>
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<td>1.49</td>
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<td>5.75</td>
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<td></td>
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Tungsten oxide based Hydrogen and Methane Gas Sensors

References


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