CHAPTER 5:

PREPARATION, CHARACTERIZATION AND SENSING PROPERTIES OF WO$_3$ DOPED WITH V$_2$O$_5$ FOR H$_2$ GAS
ABSTRACT:

This chapter describes the historical introduction on H₂ gas sensors followed by our work on the studies of H₂ gas sensors based on WO₃. Addition of small amount of metal oxide i.e. V₂O₅ (Vanadium pentoxide) to base WO₃ not only is found to make the element highly selective to H₂ but significantly enhance the sensitivity of the sensor element to H₂ and also reduces the response time. The sensor element has been tested for cross selectivity to other reducing gases and confirmed unambiguously to be specifically sensitive to hydrogen gas. Different analytical techniques are used to establish the mechanism of sensitivity specifically to H₂.
5.1 HISTORICAL INTRODUCTION ON H₂ GAS SENSORS:

The need for making devices to sense and detect gases like hydrogen was felt ever since the advent of industrialization. It shows potentials for industrial applications, such as for combustion process control, H₂ leak alarm etc. The following text gives a summary of the early attempts made to come out with a suitable H₂ gas-detecting device.

A H₂ gas sensor that can replace catalytic combustion sensors used to detect leaks in the liq was studied by Roe, G. W. et al. [1] H₂ transfer systems at Kennedy Space Center was developed. A fluidic sensor concept, based on the principle that the frequency of a fluidic oscillator is proportional to the square root of the mol. wt. of its operating fluid, was utilized. To minimize sensitivity to pressure and temperature fluctuations, and to make the sensor specific for H₂, 2 oscillators are used. One oscillator operates on sample gas contg. H₂, while the other operates on sample gas with the H₂ converted to steam. The conversion is accomplished with a small catalytic converter. The frequency difference is taken, and the H₂ concentration computed with a simple digital processing circuit. The output from the sensor is an analog signal proportional to the H₂ content. The sensor is accurate and insensitive to severe environmental disturbances and is specific for H₂ even with large He concentration in the sample gas.

Miura et al. [2] studied the p.d. across solid-electrolyte proton-conductor
membranes, such as Nafion membranes, was measured to detect H$_2$ in air and N$_2$. A Nafion membrane provided the best characteristics for a H$_2$ gas sensor.

A H$_2$ gas sensor with a piezoelectric quartz crystal coated with a thin Pd film was developed by Mizutani et al. [3] for detection of small amounts of H$_2$ in inert gases. The principle of detection by a piezoelectric crystal is that the frequency of vibration of an oscillating crystal decreases with an increase in mass of a coating material on its surface. The gas is adsorbed selectively by a coating on the crystal surface, thereby increasing the mass on the crystal and decreasing the frequency. Sorption and desorption cycles of H$_2$ exhibit exponential curves. Frequency shift (F), response, and recovery time were calculated from the curves. This sensor showed relatively slow response at room temperature; however, the frequency shift had a linear relation with the partial pressure of H$_2$ (250-5000 ppm H$_2$ in N$_2$) at room temperature. Several parameters (flow rate, temp., and interferences of other gases) were investigated; no interferences were observed due to the presence of CH$_4$, CO$_2$, and SO$_2$ as impurities in the inert gas and the effect of flow rate was scarcely noticeable. The F, response, and recovery time depend on temp. (25-100 °C); they decrease at higher temps. The effect of temperature is a trade-off between sensitivity and response or recovery time. At room temp. and a low concentrations of H$_2$ (250-5000 ppm), the rates of H$_2$ sorption and desorption in and from Pd film are expressed by first-order kinetics involving surface migration as proposed by Bucur and Messca (1975) for high temp. (80 °C) and higher H$_2$.
concentration (2.0-70.9 torr) processes.

Yong-su Oh et al. [4] fabricated an optically-detectable H₂ sensors of Pd/WO₃ by r.f. magnetron sputtering technique, and the sensing characteristics were investigated in terms of the effect of variety of sputtering conditions, including the difference in the target material used. The sensors prepared by using W metal plate as the target showed higher sensitivity and faster response rate than that prepared by using WO₃ powder as the target.

Smith shows [5] the stability sensitivity and selectivity of r.f. sputtered gold-doped tungsten trioxide films for gas-sensing applications. The WO₃ films sensing properties, such as electrical conductivity and carrier type, concentration and mobility, have been measured it is found that in order to improve the WO₃ film stability sensitivity and response time, it is necessary to subject the as-deposited films to a heat treatment or 'Activation' process. This process enables concentrations of less than one part per billion (ppb) of hydrogen sulfide (H₂S) in air to be measured reproducibly the film are exposed to several interference gases are found to be weakly sensitive only to hydrogen (H₂) however, this is not expected to be problematic in H₂S sensing applications.

Thin SnO₂ films for H₂-gas-sensor application were prepared by r.f. magnetron sputtering by Michel. H. et al. [6] The temp.-dependent elec. cond. is measured in humid synthetic air without and with hydrogen. A model for the elec. cond. was developed, which consists of two parts, one of them a simple
exponential function. The authors suggest this is caused by a strongly doped interdiffusion layer. An influence of three different glass substrates was observed. The subtraction of the interface conductance leads to an $H_2$ sensitivity that depends less on the sensor temperature.

Michel, H. et al. [7] studied thin SnO$_2$ films, prepared for $H_2$-gas sensor application by RF magnetron sputtering onto different SiO$_2$ based glasses. ARXPS and sputter-AES measurements were performed to evaluate the compn. at SnO$_2$-TiN-Au contacts as well as the depth-dependent compn. at SnO$_2$-substrate-interfaces. A Ti-oxynitride compound was identified as a boundary layer between SnO$_2$ and TiN. Enrichments of the substrate components Ba, B or Na was observed at the interface of SnO$_2$ and glass. These observations explain the activated interface conduction path by a strongly doped interdiffusion layer.

The gas sensing properties of Pd-gate MOS $H_2$ gas sensor were investigated by Dwivedi et al. [8]. The Pd-gate MOS gas sensor was fabricated on p-type $<111>$ Si wafer having resistivity 3-5 cm. The wafer was properly cleaned using std. cleaning procedures used in Si technology. The structure of the device was completed by evaporiting TiO$_2$ over Si wafer and subsequent Pd front with Al back metalization. The capacitance and conductance vs. gate bias voltage characteristics of the fabricated device were studied upon exposure to $H_2$ in Ar atmosphere. The fabricated MOS capacitor with TiO$_2$ as an insulator showed a significant change in capacitance and conductance with parallel shift in peak conductance position at room temp., when exposed to $H_2$ at various
concentrations starting from 1-4% in Ar ambient with measurement frequencies 1 MHz and 100 kHz.

Dong, L. F. et al. [9] prepared Nanometer ZnO, ZnO-Fe, by H₂+Ar arc plasma method. Compared with coarse-grained ZnO, nano-ZnO evidently possesses grain-size effect and the operating temperatures shift toward a lower temperature. The sensitivity of ZnO increases with decreasing grain size. Nano-ZnO exhibits higher sensitivities to LPG and C₂H₆ than to H₂ and CO. Compared with nano-ZnO and ZnO-Ag, nano-ZnO-Fe-Ag exhibits excellent selectivity to H₂ with high sensitivity at < 200 °C and the response time is <15s. Thus, nano-ZnO-Fe-Ag holds promise as a low-power selective H₂ gas sensor.

Zhu, W. et al. [10] prepared a Ferroelectric (Ba₀.₆₇Sr₀.₃₃)Ti₁₀₂O₃ thin films by the sol-gel technology and characterized using TGA, DTA, x-ray diffraction, at force microscopy (AFM), dielectric characterizations, and gas sensing measurements. These (Ba₀.₆₇Sr₀.₃₃)Ti₁₀₂O₃ thin film gas sensors are made on Si substrates to detect hydrogen and related hazardous gases. In such a metal-ferroelect.-metal-silicon (MFMS) structured H₂ gas sensor, dissociated hydrogen H⁺ ions are accumulated at the metal-ferroelec. BaTiO₃ interface, as a result, a dipolar potential is built up in the device. The high dielectric constant of (Ba₀.₆₇Sr₀.₃₃)Ti₁₀₂O₃ thin films enhances the induced charge at the interface, thus greatly improves the sensitivity of H₂ gas detection. The H₂ gas sensing properties of these ferroelec. thin film gas sensors are closely correlated with their microstructure and the gas sensitivity to hydrogen at 1000 ppm, indicating
great promise to fabricate large-scale, Si based ferroelectric gas sensors. Based on the best knowledge, it is the 1st time in the literature to report this type of ferroelectric thin film device for the hydrogen gas sensor application.

A highly selective $\text{H}_2$ gas sensor was developed by new cosmos Co. Ltd. [11] based on "Hot Wire Type" gas sensor. Tin oxide was sintered in a bead (0.50 mm diam.) covering over a platinum wire (0.02 mm) coil. A dense layer with ca. 0.1 mm in depth near the surface of the porous bead was formed by chemical vapor deposition (CVD) of hexamethyldisiloxane (HMDS). The dense layer functioned as "mol. sieve", thereby the diffusion of gases with large mol. diams. except for $\text{H}_2$ was effectively controlled, resulting in a prominent selectivity to $\text{H}_2$. A resistance against a strong reduction with $\text{H}_2$ due to the system was improved by addition of cerium oxide. The $\text{H}_2$ selective gas sensor thus obtained had a significantly minor humidity dependence and a prominent long term stability.

The same company [12] was developed a highly selective $\text{H}_2$ gas sensor based on a 'hot wire type' gas sensor com. available. Sn oxide semiconductor was sintered in a bead (0.5 mm in diam.) covering over a Pt wire (0.02 mm in diam.) coil. The gas sensor was operated by a bridge electric circuit. A dense layer of 0.1 mm in depth near the surface of the porous bead, was formed by CVD of hexamethyldisiloxane (HMDS). The dense layer functioned as a 'mol. sieve', thereby the diffusion of gases with large mol. diams., except for $\text{H}_2$, was effectively controlled, resulting in a prominent selectivity for $\text{H}_2$. However,
diffusion control of O\textsubscript{2} caused a strong H\textsubscript{2} reduction of the Sn oxide in the inner layer covered with the dense layer, resulting in decay in sensor output and irreversible reduction of the H sensitivity (deactivation of Sn oxide). As a countermeasure against the damage, addition effect of Ce oxide from 0.5 to 5.0 at.% was studied. The H\textsubscript{2} selective gas sensor thus obtained, had a significantly minor humidity dependence and a prominent long term stability.

A highly sensitive and selective H\textsubscript{2} sensor based on In\textsubscript{2}O\textsubscript{3} was developed by New cosmos electric Co. Ltd. [13] By use of a hot wire type semiconductor sensor com. available. The powder of In\textsubscript{2}O\textsubscript{3} was sintered in a bead (0.50 mm diam.) covering over a platinum wire (0.02 mm diam.) coil. Then, a SiO\textsubscript{2} accumulated dense layer was formed near the surface of the porous bead by chem. vapor deposition of hexamethyldisiloxane. The sensitivity to H\textsubscript{2} was about forty times as large as a current sensor based on SnO\textsubscript{2}. The sensor had also a very high selectivity to H\textsubscript{2} (e.g., the sensitivity to 5 ppm H\textsubscript{2} was equal to that to 1000 ppm C\textsubscript{2}H\textsubscript{5}OH). Moreover, the sensor had a minor humidity dependence and a long term stability (about 900 days). Thus, indium oxide was a suitable material for the highly sensitive and selective H\textsubscript{2} sensor.

Ferroelectric (Ba0.67Sr0.33)Ti\textsubscript{1.02}O\textsubscript{3} thin films were prepared by Zhu. W. et al. [14] by the sol-gel technology and characterized using TGA, DTA, XRD, TEM, dielectric characterizations, and gas sensing measurements. The (Ba0.67Sr0.33)Ti\textsubscript{1.02}O\textsubscript{3} thin film devices are made on Si substrate to detect H\textsubscript{2} gas and to study gas sensing mechanism. Experimental results show that the
Schottky I-V behavior appears in these Pd/amorphous (Ba,Sr)TiO₃ thin film/metal capacitive devices, and that the enhanced voltage shift as large as 4.5 V at 1042 ppm H₂ in air was observed. Compared with the available data in the literature, this obtained value of voltage shift in our experiment is 7 times larger than the best one reported under similar testing conditions. The H₂ induced voltage shift is closely correlated with the microstructure of ferroelectric thin films and the enhancement of this polarization potential is mainly attributed to the high dielectric constant of amorphous ferroelectric thin films. In this paper, we report our experimental results of this new H₂ gas sensor and discuss the relationship between microstructure and H₂ gas sensitivity in these ferroelectric thin film sensors.

Katsuki, A. et al. [15] made a highly selective H₂ gas sensor by formation of a dense layer functioning as a "mol. sieve" near the surface of a sintered SnO₂ layer. The dense layer (the depth of ca. 0.1 mm) was formed by chemical vapor deposition of hexamethyldisiloxane (HMDS). While, a serious reduction of the H₂ sensitivity was always caused by a deactivation of SnO₂ with H₂. Such a serious problem was removed by an addition of CeO₂ (2.0 %), thereby the oxidation activity of SnO₂ was controlled. The H₂-selective gas sensor thus obtained had an extremely minor humidity dependence and a prominent long-term stability.

Deng, J. et al. [16] studied hydrogen transport phenomenon and its mechanism in a new type of Pd/ferroelectric BST/metal hydrogen gas sensor. This new electronic device is fabricated with an amorphous ferroelectric BST thin film
using the sol-gel deposition technology, and characterized by XRD, AFM, and gas sensing measurements. The conduction properties of these amorphous BST thin films are carefully studied. The interface controlled leakage current behavior confirms the previously proposed surface-blocking model as the main mechanism for this new type of hydrogen gas sensor using ferroelectric amorphous thin films. The sensitivities of different hydrogen concentrations diluted in air and in N₂ are also presented.

Yasuhiro Shimizu et. al [17] prepared TiO₂ films and Pd metal have been investigated at 250-500 °C under reverse and forward bias conditions. A TiO₂ films (A-TiO₂) oxidized anodically in a H₂SO₄ solution had nano-holes of 50-130 nm in diameter and exhibition the highest H₂ sensitivity among the films tested, especially under reverse bias conditions. A-TiO₂ was less sensitive to CO, but its H₂ sensitivity was decreased by the coexistence of water vapors.

S. G. Ansari, et al. [18] developed MoO₃ doped SnO₂ nano-particles by using Sol-gel method with 0.1 molar solutions of SnCl₄·5H₂O and MoO₃ with different doping concentration from 5.03 × 10⁻⁴ to 5.04 × 10⁻³ mol. The average grain size varies from 12 to 80 nm obtained by varying calcination temperature from 300 to 900 °C. Thick film samples, of about 25 mm thickness, were tested for H₂ in the concentration range of 15 to 1000 ppm in ambient air. The sample exhibit selective response to H₂ at 240 °C. The sensitivity increases with doping concentration for H₂. The response and recovery time is less than 10 seconds.
Zhu et al. [19] studied (Ba,Sr)TiO$_3$ and Pb(Zr,Ti)O$_3$ thin films, prepared for hydrogen gas detection using the sol-gel and RF sputtering technology. Experimental results show that the hydrogen-sensitive leakage current is influenced significantly both by the microstructure of thin films and by their compositions. The amorphous BST and PZT thin films exhibit the promising electrical properties for hydrogen detecting devices. Studies on the transient response and impedance spectra provide substantial evidence for our proposed model regarding proton-blocking at Pd/ferroelec. interface, and the gas sensing mechanism is further elucidated.

Wang et. al [20] prepared Fe$_2$O$_3$ element loaded with 6 wt. % Ag$_2$O is very sensitive to H$_2$ at 320 °C, while it is also sensitive to many other gases, especially C$_3$H$_8$OH. The element is highly sensitive and selective to H$_2$ and LPG, after it is modified with the surface-coat of Al$_2$O$_3$ containing 1.5 wt. % PtO. The response of this element to H$_2$ and C$_4$H$_{10}$ is rather rapid (only 4 and 6 s, respectively), and its resistance only changes 8.9% even when the ambient relative humidity varies broadly (from 10 to 98%).

Many other researchers (21-34) have also been worked on hydrogen gas sensors.
5.2 STUDIES ON H₂ GAS SENSORS:

As mentioned in chapter 4, WO₃ is an excellent material for sensor fabrication but the main disadvantage is its lack of selectivity, in that it exhibits conductance change on exposure to many reducing gases as discussed earlier. A degree of selectivity could be conferred by careful control of sensor operating temperature and use of specific additives. It is well known that addition of small amount of metal oxide, V₂O₅ to the element can promote not only gas sensitivity but also the rate of response. Such promoting effects are undoubtedly related to the catalytic additives of the metal for the oxidation of inflammable gases. In base WO₃ prepared from Ammonium tungstate, V₂O₅ with different wt. % is added and the sensor element has been tested for gas sensing mechanism in presence of different reducing gases. The method of preparation of WO₃ from Ammonium tungstate is described in the chapter 4.

5.3 SYSTEM: WO₃ : V₂O₅ :-
5.4 PREPARATION OF WO$_3$ : V$_2$O$_5$ :-

Calculated quantity of WO$_3$ powder is mixed with required amount of vanadium pentoxide (V$_2$O$_5$) in an agate mortar. The mixture is thoroughly ground by using distilled alcohol as solvent, followed by evaporation to dryness and calcined at 650 °C for 5 hours. The compound is then characterized for its structural properties. The powder is then mixed with a few drops of tetraethyl ortho silicate (TEOS) and the resulting paste is applied onto alumina tube substrates attached with two platinum electrodes 8 mm apart. The elements are sintered at 750 °C for 2 hrs. For gas sensing experiments the element is kept in an apparatus through which air or sample gas is let in.

5.5 CHARACTERIZATION :

The WO$_3$ : V$_2$O$_5$ powder obtained has been characterized for its structural properties by studying the temperature of decomposition of WO$_3$ : V$_2$O$_5$ , with the help of Differential Thermal Analysis (DTA), X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), and Scanning Electron Microscopy (SEM) are used for structural and morphological studies.
5.5.1 DIFFERENTIAL THERMAL ANALYSIS:

Simultaneous TG - DTG - DTA was performed in air on a Mettler Toledo Star TGA/SDTA 851 system apparatus (Pt crucibles, Pt - Pt / Rh thermocouples) with the heating rate of 10 °C min⁻¹ from 25 °C to 900 °C on the ammonium tungstate confirm the results given below.

Fig. 5.1 shows the thermogravimetry patterns of the WO₃ prepared from ammonium tungstate. The mass decrease observed for this sample below 200 °C is due to the loss of water of hydration, that between 50 °C and 450 °C to the elimination of both constitutional water (from the six OH⁻ groups bounding to W) and NH₃. In DTA pattern, the endothermic peak observed around 270 °C is attributed to the loss of both constitutional water and ammonia.

5.5.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT - IR):

The analysis of the vibrational spectra in the skeletal region has been performed with FT-IR. The IR spectrum of WO₃ : V₂O₅ (10 Wt.% ) Sample is calcined at 650 °C for 5 hrs. are reported in Fig. 5.2(a-b).

The spectra 5.2(a-b) show the presence of monoclinic WO₃. They show the IR bands at 980 cm⁻¹ which falls in the region typical of the stretching of W =
Fig. - 5.1 DTA Spectrum of the Sample of WO₃
Fig. 5.2 FTIR Spectra of (a) WO$_3$ (Prepd. from ammo. tung.)

\[ \text{for } 4000 \to 400 \text{ cm}^{-1} \]
O bonds having a double bond character, such as those characteristic of WO₃ hydrates. The broad IR absorptions at 900-800 cm⁻¹ fall in the regions corresponding to the vibrations of the type W-O-M (M=W and in Fig. 5.2(b) M=W or V) stretching the deformation modes, respectively, as in the case of different polymorphic forms of crystalline WO₃ and tungstic polyoxo anions. In the high frequency region all the spectra show a broad adsorption centered near 3500 cm⁻¹ attributed to H-bonded OH groups.

5.5.3 X-RAY DIFFRACTION (XRD):

X-ray diffractometer (model: SIEMEN D 5000) with copper target, Kα radiation (λ=1.5406 Å) was used for phase identification, where the diffracted intensities were recorded as a function of 2θ. In order to obtain high resolution and low noise, the measurements have been performed in Bragg Brentano mode using 0.6 mm/ Ni/ 0.1 mm slits. Fig. 5.3(a) is the X-ray diffraction pattern of the WO₃ powder prepared from ammonium tungstate calcined at 650 °C for 5 hrs. The spectrum shows complete formation and all the lines agree with those of reported values.

While Fig. 5.3(b) is the spectra which corresponds with the WO₃ with 10 wt. % loading of V₂O₅ which shows an extra peak other than that of WO₃ in the region of 2θ = 20.5 which is in good agreement with the reported value (JCPDS data No. 77-2418).
Fig. 5.3 XRD Pattern of the

a) WO$_3$ Prepared from Ammonium tungstate.  
b) WO$_3$: V$_2$O$_5$ (10 Wt. %)
5.5.4 SCANNING ELECTRON MICROSCOPY (SEM):

Scanning Electron Microscopy (SEM) was used to establish the morphology and to evaluate the particle size distributions. Calcination leads to the formation of agglomerates due to the establishment of electrical contact between themselves.

SEM pictures of pure WO₃ : V₂O₅ (10 Wt. %) are shown in the Fig. 5.4. The method employed for this involves calcination from 550-950 °C. The observations from all these micrographs are summarized as follows.

(a) For WO₃ : V₂O₅ (10 wt. %) calcined at 550 °C and 650 °C, the aggregates are loose. At 550 °C calcination the particles are well dispersed and the ultimate particle size is 0.1 μm.

(b) In case of 650 °C calcination composition, the ultimate particle size does not seem to increase but the particles are coming closer. Individual crystallites are clearly visible and the ultimate particle size is 0.25 μm. This observation is some what similar to that of pure WO₃ prepared from ammonium meta tungstate.

(c) Calcination at 750 °C makes the particle size uniform, and spherical. Whereas in case of pure WO₃ (Ammonium meta tungstate) particles are needle
Fig. 5.4. SEM Micrographs of $\text{WO}_3 : \text{V}_2\text{O}_5$ (10 wt.%)
Calcined at (a) 550 (b) 650 (c) 750 (d) 850 & (e) 950°C
shaped. This may be the effect of addition of $V_2O_5$. The average crystallite size is 0.25 μm.

(d) At 850 °C the SEM micrographs are clear with well-defined crystallites. The ultimate particle size is above 0.6 μm and each of the agglomerates is of an average size of 3-4 μm.

(e) At 950 °C calcination shows well-formed crystallites of WO$_3$ which are characterized by the multifaced spherical crystallites.

Another observation is that the crystallite sizes in WO$_3$ : $V_2O_5$ (10 wt. %) is smaller than that of pure WO$_3$ even though the physical appearance of each is qualitatively similar. This means the presence of $V_2O_5$ in WO$_3$ may be preventing the grain growth of WO$_3$ and thereby acting as a grain growth inhibitor.

### 5.6 GAS SENSING CHARACTERISTICS OF WO$_3$ : $V_2O_5$ :-

Fig - 5.5 shows the gas sensing characteristics for the composition of WO$_3$ - $V_2O_5$ (5 wt %) powder. This sensor element shows a higher sensitivity to $H_2$ and LPG. The sensor element starts sensing $H_2$ at a very low operating temperature of 175 °C and goes on increasing upto 300 °C. While the maximum sensing to LPG is 0.86 at 300 °C. Similarly the maximum sensitivity to LPG is found to be 0.8 at 300 °C. The other gases i.e. CO, CO$_2$, and NO$_2$ shows 0.54, 0.31, 0.47 at the range of 275 - 300 °C operating temperature.
Fig. 5.5. Sensitivity Vs Operating Temperature for WO$_3$ : V$_2$O$_5$ (5 wt. %)
for a) LPG, b) H$_2$, c) CO, d) CO$_2$, e) NO$_2$

Fig. 5.6. Sensitivity Vs Operating Temperature for WO$_3$ : V$_2$O$_5$ (10 wt. %)
for a) LPG, b) H$_2$, c) CO, d) CO$_2$, e) NO$_2$
Fig. 5.6 shows the sensitivity versus operating temperature to gas sensing characteristics of WO$_3$ - V$_2$O$_5$ (10 wt. %) powder. This sensor element shows an exceptionally high sensitivity to H$_2$ at a very low operating temperature. The sensor starts sensing H$_2$ at about 175 °C and reaches a maximum of 0.86 at about 250 °C. This sensor element shows sufficient selectivity towards H$_2$ at 200 °C. The sensitivity of other gases at an operating temperature of 200 °C is much lower than H$_2$ as 0.34, 0.26, 0.03 as 0.31 to LPG, CO, CO$_2$ and NO$_2$ respectively.

Fig. 5.7 shows the gas sensing characteristics of WO$_3$ - V$_2$O$_5$ (15 wt. %) powder. This sensor element shows good response towards H$_2$ and LPG. The sensor shows maximum sensing to H$_2$ and LPG of 0.78 and 0.81 at 300 °C operating temperature. While other gases are sensed to much lesser extent i.e. 0.32, 0.21 and 0.27 for CO, CO$_2$ and NO$_2$ at 300 °C.

From the above experiments it is concluded that V$_2$O$_5$ as a dopant in WO$_3$ shows better gas sensitivity to H$_2$. Out of three compositions, the best composition for the gas is found to be WO$_3$ - V$_2$O$_5$ (10 wt. %). For this composition the maximum sensitivity to H$_2$ rises from 175 °C onwards and maintain this even upto 350 °C. Hence this optimum composition has been studied further to see the effect of noble metal on sensitivities to H$_2$. 
Fig. 5.7. Sensitivity Vs Operating Temperature for WO₃ : V₂O₅ (15 wt. %)
for a) LPG, b) H₂, c) CO, d) CO₂, e) NO₂
5.6.1 EFFECT OF NOBLE METAL ON SENSITIVITY:

The next step is to add (incorporate) the noble metal to increase the sensitivity. Fig. 5.8 shows the sensitivity versus operating temperature for sensor element $\text{WO}_3 - \text{V}_2\text{O}_5$ (10 wt. %)-Pd (with different wt. % i.e. 0.5, 1.0 and 1.5 wt. %) from 100 °C to 350 °C operating temperature. It is found that in case of 1 wt. % Pd the sensitivity to $\text{H}_2$ is much greater i.e. 0.98 at 200 °C while in case of 0.5 and 1.5 wt. % Pd the sensitivity to $\text{H}_2$ is 0.85 and 0.73 at 200 °C respectively.

From the above experiments it is found that the best composition for maximum sensitivity for $\text{H}_2$ is found to be $\text{WO}_3 - \text{V}_2\text{O}_5$ (10 wt. %)-Pd (1 wt. %) sintered at 750 °C for 2 hrs.

The above sensor element was checked for cross sensitivity at different operating temperature for other gases.

Fig - 5.9 shows the cross sensitivity to $\text{WO}_3 - \text{V}_2\text{O}_5$ (10 wt. %)-Pd (1 wt. %) system as a function of operating temperature. The sensor shows good selectivity towards $\text{H}_2$ as compared to the other gases. At 200 °C the sensitivity to $\text{H}_2$ is 0.98 while that of other gases viz. LPG, CO, CO$_2$ and NO$_2$ is 0.18, 0.11, 0.01, 0.08 which is much less as compared to $\text{H}_2$. The saturation sensitivity of 0.98 for $\text{H}_2$ was at a temperature of 200 °C.
Fig. 5.8. Sensitivity Vs Operating Temperature for $\text{WO}_3 : \text{V}_2\text{O}_5$ (10 wt. %)
With Different wt. % of Pd for $\text{H}_2$. 
Fig. 5.9. Sensitivity Vs Operating Temperature for WO$_3$ : V$_2$O$_5$ (10 wt. %) : Pd (1 wt. %) for a) LPG, b) H$_2$, c) CO, d) CO$_2$, e) NO$_2$
5.6.2 EFFECT OF CONCENTRATION OF H₂ IN AIR:

H₂, which has been used for studies of sensitivities as a function of concentration, is diluted as described in chapter 4.

The sensitivity of sensor to various concentrations of H₂ has been plotted in Fig. 5.10. This is called as the calibration curve. It is seen that the elements of WO₃ : V₂O₅ (10 wt. %) - Pd (1 wt. %) reaches the saturation value of sensitivity for concentration of 800 ppm. The sensor is able to detect upto 200 ppm H₂ with reasonable sensitivity.

5.6.3 RESPONSE CHARACTERISTICS:

Fig - 5.11 shows the response characteristics of WO₃ : V₂O₅ (10 wt. %) Pd (1 wt. %) system. It is clearly seen that the sensor element reaches its maximum value of sensitivity in less than 1.5 minute. But this system take lot of time i.e. about 15 minute to come back.
Fig. 5.10 Sensitivity as a Function of Concentration of H₂ in Dry Air of the WO₃ : V₂O₅ (10 wt. %) : Pd (1 wt. %) Sensor Element at 200 °C.

Fig. 5.11. Response Characteristics of WO₃ : V₂O₅ (10 wt. %) : Pd (1 wt. %) for H₂.
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