



CHAPTER 6 :

SUMMARY AND CONCLUSIONS

SUMMARY

Gas sensors using oxide semiconductors have been subjected to extensive research and development and have now grown to be important devices for detection the leakage of several toxic and inflammable gases. In recent years much research efforts has been directed towards the detection of low concentration of gases. To detect such low level of gases, the sensors should be highly upgraded in forms of sensitivity, selectivity, reproducibility and stability. Although semiconductor gas sensors have so far been developed mostly by empirical research further development and innovation seems to be impossible without a fundamental understanding of the gas sensing mechanism and sensor design principles involved which have so far largely been ignored.

Hydrocarbon gases are being widely used as a fuel for domestic and in industry as a clean source of energy for burning. However, they are potentially hazardous because of a high possibility of explosion accidents caused due to leakage. This has resulted in an increased demand to develop sensors to detect these hydrocarbon gases and hence special attention has been focussed on the development of sensors to detect Liquid Petroleum Gas (LPG).

WO_3 is known to be a n-type semiconductor with a band gap of 2.6 eV due to vacancies at oxygen lattice sites. Oxygen adsorbates available on the

surface react with reducing gases resulting an increase in conductivity. But the problem is that similar reactions also may occur on the surface with other gases. Being aware of these limitations of using WO_3 as the base material for gas sensors many methods are being adopted to impart selectivity to a particular gas. It is known that addition of small amounts of noble metals such as Pd, Pt to WO_3 can promote not only the gas sensitivity but also the rate of response. A degree of selectivity could be conferred by careful control of sensor operating temperature and use of specific additives. Since preparation conditions are known to strongly influence the gas sensing characteristics of sensors, the base semiconducting material WO_3 has been prepared by different methods to see the effect of microstructure, crystallite size and porosity on the sensitivity to various reducing gases. The WO_3 has been characterized by various techniques such as Differential Thermal Analysis (DTA), X-Ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) for structural and morphological studies.

We examined the effect of starting material on the gas sensitivity. Results on commercially available WO_3 and WO_3 obtained from phospho tungstic acid and ammonium tungstate have been compared. The sensitivity as well as the selectivity of WO_3 prepared from ammonium tungstate is found to be exceptionally good. So, for further study we used WO_3 prepared from ammonium tungstate. Thereafter the effect of calcination on the sensitivity was studied, and the best result was obtained at a calcination temperature of $650\text{ }^{\circ}\text{C}$. Similarly the

effect of sintering temperature on the sensor element with tetra ethyl ortho silicate as a binder was studied, at 750 °C, TEOS get decomposed and increases the strength of binding and ultimately increases the sensitivity. With the aim of improving the sensitivity and imparting selectivity, different oxides have been incorporated into WO_3 and the gas sensing characteristics were studied. Addition of small amount of metal oxides to WO_3 not only is found to make the element highly sensitive to LPG but also reduce the response time. Several systems were tried to obtain the best composition for making selectively for LPG and H_2 .

We examined sensing characteristics of $WO_3 : La_2O_3$ system in which different weight percentages of La_2O_3 is loaded in based WO_3 . We found that with increase in weight percentage of La_2O_3 , sensitivity also increases. The sensor element $WO_3 : La_2O_3$ (15 wt. %) shows good sensitivity (0.77) towards LPG at 300 °C. We have also checked for cross sensitivity to H_2 , CO, CO_2 , and NO_2 but the element senses all these gases with a sensitivity of 0.43, 0.49, 0.16, 0.30 at 300 °C respectively.

Further we studied $WO_3 : SnO_2$ system in which different weight percentages of SnO_2 is loaded in base WO_3 . It is found that with 10 wt. % of SnO_2 in WO_3 shows high sensitivity (0.80) to LPG at 325 °C. But the sensor element shows sensitivity of 0.40, 0.47, 0.12 and 0.12 to H_2 , CO, CO_2 and NO_2 respectively at 325 °C. It was observed that with further increase in SnO_2 concentration (15 wt. %), the sensitivity decreases.

A comparative study of the gas-sensing characteristic of WO_3 with different loadings of In_2O_3 showed that 5 wt. % loading is optimum. With this composition we have checked for cross sensitivity to LPG, H_2 , CO , CO_2 and NO_2 . This sensors element shows a sufficient selectivity towards LPG at a very low operating temperature of $200\text{ }^\circ\text{C}$. The sensitivity to LPG is above 0.70 at $200\text{ }^\circ\text{C}$ while the sensitivity of other gases (H_2 , CO , CO_2 and NO_2) at the same operating temperature is negligible. So for further work we used the $\text{WO}_3 : \text{In}_2\text{O}_3$ (5 wt. %) composition.

In addition, the effect of incorporation of different weight percentages of noble metals on the sensitivity and selectivity has also been studied. It was observed that 1 wt. % Pd in $\text{WO}_3 : \text{In}_2\text{O}_3$ shows the sensitivity of 0.90 at $250\text{ }^\circ\text{C}$ operating temperature. Similarly the effect of addition of different weight percentages of Pt on sensitivity as well as selectivity of $\text{WO}_3 : \text{In}_2\text{O}_3$ (5 wt. %) sensor element has been studied. It is seen that the sensors response to LPG at $200\text{ }^\circ\text{C}$ is 0.97 for 0.5 wt. % of Pt. The sensor element has been tested for cross selectivity to other reducing gases and confirmed unambiguously to be specifically sensitive to LPG gas. The effect of Pt is seen not only increasing the sensitivity to LPG considerably but also the rate of response. Different analytical techniques are used to establish the mechanism of sensitivity.

We have also developed H_2 gas sensor based on semiconducting oxide, WO_3 . Addition of small amount of V_2O_5 to WO_3 not only is found to make the

element highly selective to H_2 but significantly enhance the sensitivity of the sensor element for H_2 but also reduce the response time. We have examined the $WO_3 : V_2O_5$ system with different weight percentages of V_2O_5 in base WO_3 . It was found that the sensor element with 10 wt. % of V_2O_5 shows high sensitivity (0.85) to H_2 at 200 °C operating temperature. So for further study, the optimum composition ($WO_3 : V_2O_5$ 10 wt. %) was chosen.

The effect of addition of different weight percentages of Pd to the sensor element on sensitivity, selectivity as well as rate of response has been studied. It was observed that with 1.0 wt. % of Pd the sensitivity to H_2 gas is 0.98 at 200 °C. Further, the sensor element was examined for cross sensitivity to LPG, CO, CO_2 and NO_2 , which are found to be 0.18, 0.11, 0.01 and 0.08 at 200 °C respectively. From the SEM studies, it is seen that the grain size of WO_3 increases with increasing in the calcination temperature while with addition V_2O_5 in WO_3 , the grain size get decreases. This implies that V_2O_5 is capable of inhibiting the growth of WO_3 crystallites to some extent.

FUTURE PLANS :

Most semiconductor gas sensors make use of changes in electrical conductivity, which is a phenomenon caused mainly by the adsorption and desorption of chemical species on their surfaces. The surfaces of semiconductor gas sensor are covered with the chemisorbed oxygen species on their surfaces and their amount dictates the conductivity of the sensor surface. Accordingly, it is difficult to distinguish among gases exhibiting similar adsorption behaviour and similar reactivity with chemisorbed oxygens. On the other hand, the sensing characteristics of heterojunction type of gas sensors is good proposition. The advantage of using, p/n junctions for gas sensors is the different characteristics of gas adsorption on various p and n type semiconducting surfaces could be used to distinguish gas species effectively.

From our studies we have definitely established that the crystallite size is one of the major factors governing the extent of sensitivity in these chemical sensors. It has been our endeavor to reduce the crystallite size to the best and smallest possible with the available techniques by adopting different synthesis routes. These studies have given some very encouraging results as far as the gas sensing characteristics are concerned. In future I would like to try some more novel methods which could be adopted to obtain these materials in the form of nanoparticles or nanocrystals. This field of research is an upcoming area of

science wherein lies the future to synthesize materials with extraordinary physical, chemical and of course gas sensing properties.