Chapter 7
Conclusions

Nowadays, much awareness has been devoted in developing sensors for monitoring the pollutants and hazardous gases in various environments. Considerable development work is being carried out in order to produce sensors that are low-cost, simple to operate, sensitive and selective to specific gases. Recently, research efforts have been strengthened world over to develop gas sensors for inflammable and toxic gases. The investigations are focused on enriching the key parameters related to this, namely, sensitivity, selectivity, rapidity of response-recovery times and the operating temperature. To develop a sensor to meet the key parameters, severe efforts are needed especially by methods such as doping, fabrication of nano-sized thin films, annealing etc.

Detection of Liquefied Petroleum gas (LPG), which is highly inflammable, is more relevant as it is widely used for many domestic purposes, automobiles and industrial requirements. Therefore, continuous monitoring of LPG becomes inevitable for the purpose of control and safety applications in both domestic and industrial fields. In addition to this in recent years, there is an increasing public concern about the air and food quality control. Therefore, the detection of CO$_2$ concentration in the low concentration range is extremely important. These applications require inexpensive and robust detection systems. In the last two decades or so, remarkable developments has been made in making new gas sensors based on semiconducting metal oxide films such as tin oxide, zinc oxide, indium oxide etc. Derived from these materials, both bulk and thin film sensors are fabricated. These devices are able to detect and monitor the presence of various gases by the adsorption of gases on the oxide material under particular conditions,
thereby a change in conductivity, which is used as a measure of the gas concentration. Such gas sensors are available for the detection of combustible gases, alcohol, carbon monoxide, ammonia etc. These gas sensors make a major impact on many different applications such as in automotive industries, oil industries and household applications.

Much of the gas properties of thin films show profound dependence on the microstructure, which depends on the method of preparation of the thin film. Spray pyrolysis is a desirable technique for the preparation of inexpensive doped tin oxide thin films. Besides the simple experimental arrangement, high growth rate and mass production capability for large area coatings make them useful for industrial as well as minor-league applications. In addition, spray pyrolysis opens up the possibility to control the film morphology and particle size in the nanometer range.

For undoped and doped SnO$_2$ films, the gas sensing performance is strongly dependent on the film microstructure. Although various parameters affect the film microstructure, we expect strong dependence of these properties on the dopants, deposition conditions and orientation of the crystallites. In the present study, elaborate efforts are carried out on semiconducting tin oxide thin films doped with Cs, Mn and La with a quest to develop cost-effective LPG sensors. The investigations are extended to the study of gas sensing properties of the deposited films towards CO$_2$. The conclusions drawn out of these studies and the scope for further investigations are elaborated in this concluding chapter.

Detailed measurements are made on the gas sensing properties of polycrystalline SnO$_2$ thin films doped with different concentrations of Cs, Mn and La at various deposition temperatures. In all the cases, the sensitivity is reported for a concentration of 1000 ppm of target gas and the response time is found to vary with dopant concentration. The
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reproducibility is ascertained by measuring the data on several samples prepared under nearly identical conditions. Studies revealed that undoped SnO\textsubscript{2} are gas sensitive but the sensitivity is poor. The effect of doping level on the gas sensing properties is investigated for films deposited at different substrate temperatures. In general, the sensors with each of the doped groups behave by and large comparable.

To the best of our knowledge the gas sensing properties of alkaline metal Cs-doped SnO\textsubscript{2} films have not been investigated before and found that Cs-doping is a potential candidate for gas sensor applications towards LPG. On Cs doping, the grain size is found to get modified and shape become altered to exhibit more surface area and gas sensing. The depletion region formed due to the adsorption of oxygen ion on the surface of small grains extend more deeply into the grains which will ultimately allow more number of gas species to replace oxygen resulting in increase in the sensitivity. Consequently, the grain boundary controlled sensing mechanism contributes best when the individual grains are small, thereby describing an increase in the gas response. The rapid change of the resistance seems to be caused both by gas species adsorption process and by the gas transport to the intergranular volume.

Voids also contribute to the sensing in the prepared films. The voids within the film structure provide conduction paths for gas molecules to flow in from the environment. Predominant orientation of crystallites contacted with gas atmosphere on the surface of the film also has some influence on the gas sensitivity characteristics.

Gas sensitivity studies on Cs doped SnO\textsubscript{2} films indicated that there is a strong influence of concentration of dopants and spray deposition temperature on the gas sensitivity of the films. The sensor holds the highest sensitivity (93.4 \%) for 2\% Cs doped SnO\textsubscript{2} samples deposited at the substrate temperature 320°C. All the Cs doped SnO\textsubscript{2}
samples exhibited a reasonably good sensitivity to LPG at an operating
temperature of 345°C.

In the case of CO\textsubscript{2} sensing, the gas that acts as an oxidizing agent
and the electrical resistance of the sensor increases on gas presence.
That is, a reverse change in resistance is observed when the samples are
exposed to CO\textsubscript{2}. The CO\textsubscript{2} sensitivity for caesium doped SnO\textsubscript{2} films is
found to decrease with increase in the concentration of caesium. The
highest sensitivity is obtained for the 2wt% Cs doped SnO\textsubscript{2} thin film
sensor operated at 360°C.

Gas detection studies reveal that Mn doped SnO\textsubscript{2} samples
exhibits the highest sensitivity (83\%) for 2 wt.% Mn doped SnO\textsubscript{2}
deposited at the substrate temperature 320°C, when the deposition
parameters almost the same as that of Cs doped SnO\textsubscript{2} samples. The
operating temperature in this case is obtained as 330°C, which is less
than that of Cs doped samples. The minimum temperature for
crystallization is also less in the case of Mn doped SnO\textsubscript{2} samples. For
both Cs and Mn doped SnO\textsubscript{2} samples, studies reveal that a
homogeneous distribution of lower concentrations of Mn in SnO\textsubscript{2} is
advantageous to enhance sensitivity to LPG.

For CO\textsubscript{2}, the Mn doped SnO\textsubscript{2} sensors exhibits an increase of
resistance and the highest sensitivity 45\% observed is for 2 wt.% Mn
doping at an operating temperature 350°C.

For La doped samples, the sensor showed maximum sensitivity
(62\%) for 1 wt.% La doped SnO\textsubscript{2} deposited at the substrate temperature
360°C and the optimum operating temperature is obtained as 350°C.
For La doped SnO\textsubscript{2} samples, the dopant dispersed on the surface of the
grains of the sensor material activates the reducing gas and allows it to
spill over on to the sensor material. Thus, the resulting change in the
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Conductance is enhanced and consequently the sensitivity is increased better when compared to pure SnO\(_2\).

The grain size of the samples is calculated and is correlated with the gas sensitivity. The difference in grain size and grain boundaries due to variation in deposition temperature and concentration of dopant in correlation with the gas sensing activity are analysed. The texture coefficients are calculated to describe the preferred orientation. The addition of dopants affects the preferential orientational growth of the films. The standard deviation is calculated to describe the structure variation and no change in the lattice parameter is observed with the doping concentration or with the deposition temperature.

The CO\(_2\) ambient increases the resistance of La doped SnO\(_2\) films and the highest sensitivity is obtained for 1wt% Mn doped films deposited at 360ºC.

Comparing the different dopants in SnO\(_2\) sensors shows that sensitivity to LPG is the highest for the sensors doped with 2wt.% Cs at a deposition temperature 320ºC followed by 2 wt.% Mn deposited at a substrate temperature 320ºC. The LPG response of La doped samples is comparatively low. The lowest operating temperature is obtained for Mn doped samples, which can be attributed to the optimization between the enhancements of reaction kinetics of oxidation of LPG with adsorbed oxygen species. The most favorable operating temperatures can be used to examine the selectivity of gas sensors and the response and recovery times.

In the presence of CO\(_2\), the sensors has been tested and evaluated. In the presence of CO\(_2\), all the dopant groups in SnO\(_2\) exhibit sensitivity with an increase of resistance while in LPG a decrease of resistance is observed. All these sensors with dissimilar dopants are less sensitive to CO\(_2\) but the response is of the same order as that of LPG.
The long-term stability of the sensors is studied after storing the sensors in humid atmosphere for 12 to 24 months. Degradation effects are less for Cs and La doped samples. However Mn doped SnO$_2$ samples show degradation effects after 12 months by showing a decrease in the sensitivity. The annealing effect of the samples under oxygen atmosphere is also investigated with a view to observe the change in gas sensitivity.

In short, the doped SnO$_2$ sensors offer high sensitivity, rapid response and recovery to LPG and CO$_2$ gases. Among the three dopants, Cs doped samples showed highest sensitivity, better long-term stability and fast response to LPG. The gas sensitivity values are in the order Cs:SnO$_2$ $>>$ Mn:SnO$_2$ $>>$ La:SnO$_2$ $>>$ pure SnO$_2$. In addition, the change in sensitivity due to aging is insignificant. Sensitivity of the films increases with increase in annealing temperature and reaches maximum at a temperature just above its deposition temperature. The stability and the abrupt change in the electrical resistance of the material in the presence of the gas evidences the application of doped SnO$_2$ thin films as gas sensors.