CHAPTER - 2

LITERATURE REVIEW

The main aim of this research work is to detect the carbon monoxide in the engine emissions by designing and developing biosensor. Hence, a review of various works related to conventional sensors and biosensors for various applications are presented in the following section. A broad classification of sensors based on the principle of operation is shown in Fig(1.17) and fig (1,18) in chapter-1.

In this chapter, a review of various types of automotive sensors is presented after a thorough literature survey. As the sensors are made up of different materials, for easy reference of these materials a periodic table is presented in Appendix- I.

2.1 Reviews on Automotive Gas Sensors

M. H. Westbrook (1985) [19] reviewed on the sensors that are used for automotive application. Various techniques and devices that are being used and developed for providing vital sensing functions required in automobile applications are discussed. Required specifications for engine and transmission (powertrain) control are listed and the accuracy over which they are required to operate are noted.

M. Haug et al., (1993),[20] reviewed on chemical sensors based upon polysiloxanes and a comparison has been made between optical, quartz microbalance, calorimetric, and capacitance sensors. They used to monitor changes of thicknesses $\Delta d$, masses $\Delta m$, temperatures $\Delta T$, and capacitances $\Delta C$ with coated layers of chemically sensitive polysiloxanes. They tested as prototype sensors to monitor organic aliphatic, aromatic, and halogenated gas components in air at different temperatures and partial pressures. They monitored changes in mass, thickness, temperature, and capacitance as independent parameters of the same polymeric sensor
material in view of the potential and discussed the advantages and disadvantages of capacitive sensors.

Jiri Janata et al., (1994) [21] reviewed on the chemical sensors. They explained various types of sensors such as thermal sensors, mass sensors, electro chemical sensors, optical sensors, their usage and applications in various fields. They reported that the attempts to achieve an exquisite selectivity of a single selective layer may not be the most cost-effective approach in the design of chemical sensors. It has been shown that sensor arrays combined with chemometrics can achieve the same or even better results at a much lower cost. Noboru Yamazoe and Noris Miura., (1994),[22] reviewed the status of research and development on Environmental gas sensing sensors. The release of various pollutants from industries, automobiles into atmosphere has been causing the global environment issues such as acid rain, greenhouse effect and ozone depletion. In their review they discussed solid electrolyte sensors for detecting air pollutants like \( \text{CO}_2 \), \( \text{NO}_2 \), \( \text{NO} \), \( \text{SO}_x \). Further they reported that gas sensors for detecting air pollutants should often operate even under hostile conditions. This requires the relevant sensors to be particularly stable against chemical and/or thermal attack. In this respect, they proposed that the ceramic gas sensors can be of more practical importance.

J D Turner and L Austin, (2000),[23] reviewed on applications and current sensor technologies with in automotive and traffic control system. They reported on sensors that control engine fuelling, ignition, transmission, breaking, traction control and also on wheel and tyre sensors enhance safe driving. They also discussed sensors for initiating the deployment of safety system such as airbags, together with transducers for disconnecting fuel pumps and vehicle batteries in the event of a crash and also on highway based sensors for measuring vehicle speed.
J.H. Visser et al., (2001),[24] reviewed on automotive exhaust gas sensing systems. They reported that the gas sensors have become an integral component of control systems for internal combustion engines to provide information for control of air-to-fuel ratio (A/F) to achieve improved vehicle performance and fuel economy as well as decreased levels of emission. They also discussed the different sensing requirements, testing procedures, environmental parameters, and need for micro system.

William J. Fleming, (2001),[25] reviewed on automotive sensors, which focused on the sensors used in production of automotive systems. Technologies that are related to major applications in powertrain, chassis and body are presented. Sensors such as rotational motion sensors, pressure and temperature sensors, exhaust gas sensors, linear acceleration sensors, etc are described.

S. Capone et al., (2003),[26] presented an overview about the principles and technologies in solid-state gas sensors. Sensor work under the principle of measuring a physical property changed by adsorption/desorption processes and chemical reactions on surface of sensing elements are discussed. Recent advances in sensor accuracy, reliability, response time etc and future trends for research and development are presented.

Qaisar Ameer et al., (2005),[27] reviewed about polypyrrole-based electronic noses for environmental and industrial analysis. The interaction of gaseous components with deposited PPy films produces change in colour, mass, work function. The principle, operation and classification of PPy are discussed. They reported that the industrial and environmental applications of PPy based ENs (electronic nose) over the past decade have been increased considerably ranging from their development stage. These devises are easy to fabricate, reasonably reliable and can be readily adopted for online and real time environmental monitoring and
industrial analysis in sensing of various substances such as water, alcoholic and non-alcoholic beverages, waste water and sewage effluents. Additionally, their low cost, ease of production and ease with which their properties can be modified by substituent to the monomers makes conducting PPy very attractive for many industrial and environmental applications. Further they reported that the PPy gas sensors are still behind in their response time, repeatability and reproducibility.

Ralf Moos et al., (2005),[28] reviewed on electro ceramic exhaust gas sensors in automotive exhaust gas systems. All automobiles being powered by gasoline combustion are equipped with at least one zirconia exhaust gas sensor (λ probe) for detection of the air-to-fuel ratio \( λ \). They also reviewed on the potentiometric as well as on amperometric zirconia exhaust gas sensors. Materials that are used for sensors and its principle are discussed.

Joseph R.Stetter et al., (2006),[29] reviewed on sensors related to Engineering Structures and Materials from Micro to Nano. They reported that the sensors are the devices that produce a measurable change in the output to a known input stimulus. This stimulus can be a physical stimulus like temperature and pressure or a concentration of a specific chemical material. The output signal is typically proportional to the input variable, which is also called the measurand. The ability of a system to see (photonic technology), feel (physical measurements), smell (electronic nose), hear (ultrasonics), think/communicate (smart electronics and wireless), and move (sensors integrated with actuators), has been progressing rapidly and suggests an exciting future for sensors. They reviewed about different sensor types and applications.

Nicola Ulivieri et al., (2006),[30] proposed a way to standardize gas sensor. The selection of sensors type is the fundamental to the success and failure of the olfactory
system performance. In their paper they reviewed the IEEE 1451 standards and the IEEE 1451.4. Mixed-mode interface, Dot 4 TEDS, standard for gas sensors, proposals, standard templates for gas sensors, custom solution within the IEEE1451.4 standard and it module for resistive gas sensors measurements. Finally, the virtual instruments to create dot, Human Machine Interface (HMI), A. Pardo et al., (2006), also reported on the gas measurement system based on IEEE1451.2 standard.

Sheikh Akbar et al., (2006),[31] reviewed on High-Tempering ceramic gas sensors. They have mentioned the Oxygen gas detection ranges in various Industrial Process. Further they discussed various types of sensors used for the detection of NOx,CO₂,CO,H₂,CH₃ and O₂. They expressed that the commercial detectors like infrared spectroscopy, gas chromatography/ mass spectroscopy (GC/MC) and chemiluminescent analysis are available with good detection limits and fast response but these instruments are bulky, expensive , need maintenance, and not portable. Further, they expressed that there is a need of miniaturized gas sensors for in-situ high temperature monitoring and feedback control for combustion optimization. They reported the results on an anatase based two sensor array for detecting CO and O₂ . In their work nonlinear regression approach, called Kernal ridge regression (KRR) was developed for modelling sensor array behaviour and to identify gas composition quantity.

Robert Bogue (2007),[32] focused and reviewed on the historical development of the Micro-Electro Mechanical system (MEMS) sensor technology and its current use in physical, gas and chemical sensing technology. These papers provide a technical and commercial in-sight into the applications of MEMS technology to physical and molecular sensors from 1960s.
S. J. Prosser, (2007), [33] reviewed on past, present and future sensors of automotive. He reported that the majority of innovations have been achieved through electronics and use of advanced sensors. Silicon microengineering, optical, and thick film, etc are the range of technologies at have been developed over the past twenty years. The environment of these sensors are continuously challenging with respect to robustness, reliability, quality and cost. He reported that the future demands are for better capability at less cost.

C Lopez-Gandara et al., (2009),[34] reviewed on the use of nano materials and YSZ based oxygen sensors for physicochemical models and the response of potentiometric oxygen gas sensors based on ion conducting electrolyte. They reported that the classical models based on reaction rates of adsorption of different gas species in the three-phase boundary sites are still useful to understand the general working principles of the sensors.

2.2 Electrochemical Sensors

M.J. Leck e, (1985), [35] discussed the development and performance of the gas sensor for heavy gas dispersion system. The gas sensing transducer used in these instruments is an electrochemical cell which gives a signal proportional to the partial pressure of oxygen in the atmosphere. Any gas species is thus detectable by the reduction in oxygen partial pressure caused by its presence. To achieve the required frequency response, an electronic signal-enhancement technique was developed. They showed that with the help of signal enhancement techniques the required frequency specification can be met by the theoretical and experimental evaluation of the frequency response of both the standard and fast-response sensors. The sensors have an excellent linear response over the 0% to 21% oxygen range, and the experimental
air/nitrogen results show that the instruments are within the specified accuracy of ±5%.

Dario Naeducci et al., (1994) [36] investigated on determination of CO in air by YSZ-based potentiometric solid state gas sensors. Two sensors were prepared with Pt and RuO$_2$ electrodes. The sensors are characterized between 350° – 650 °C with pressures ranging from 1 to 80 Pa. Emf and response times are measured in the limit range and then the results are compared. They reported that the response time at the optimal working temperature of 420 °C is sufficiently low to predict good applicability of these sensors as CO detectors.

G. W. Hunter et al., (1998),[37] proposed the use of microfabricated chemical sensors for safety and emission control applications. Conditions that include operation in harsh environments, high sensitivity, minimal size and weight, and power consumption cannot be addressed by commercial sensors. They reported that the microfabrication is being used to fabricate miniaturized sensors to measure hydrogen, hydrocarbons, etc., to overcome these drawbacks.

H.S. Hong et al., (2006),[38] studied the filter layers to suppress cross-sensitivity of NO and SO$_2$ in electrochemical (SnO$_2$) CO$_2$ sensors. The solid state galvanic cell of Na$_2$CO$_3$-SnO$_2$, Na$_2$CO$_3$-SnO$_2$-Cu, Na$_2$CO$_3$-SnO$_2$-CuO is adopted as filter material adjacent to the sensing electrodes which were investigated at 673K and 773K. They reported that CuO added filters brought not only enhanced NO filtering but also SO$_2$ filtering ability in a limited range in the detection of CO$_2$.

2.3 Metal Oxide Sensors (MOX)

W. F. CHU et al., (1991),[39] studied the thick film gas sensors with solid electrolytes. They discussed the Nasicon or Zirconia (YSZ) solid ion conductors that
are used, which has been deposited on α-alumina substrates. Thick-film potentiometric H\textsubscript{2} sensor based on Nasicon containing a Na\textsubscript{x}WO\textsubscript{3} reference electrode and a porous Pt working electrode and all-thick-film potentiometric O\textsubscript{2} sensor based on zirconia with a Pd/PdO reference electrode and a porous Pt working electrode are investigated. They reported that e.m.f of these cells depends logarithmically on the CO\textsubscript{2} partial pressure in a CO\textsubscript{2}/O\textsubscript{2} gas mixture.

G.Faglia et al., (1994),[40] reported on frequency effect on highly sensitive NO\textsubscript{2} sensors based on RGTO (Rheotaxial growth and thermal oxidation) technique, RGTO SnO\textsubscript{2} (Al) thin films. The thin films are produced by using sputtering technique. The film response was examined by Impedance Spectroscopy. A remarkable increase in the NO\textsubscript{2} sensitivity was observed by sweeping the voltage supply from d.c to 4 MHz. They reported that the frequency intervals are suitable for a selective detection of the gaseous species in the sensor array.

J.Gerblinger et al., (1994),[41] studied on cross sensitivity of various doped Strontium Titanate films to detect CO, CO\textsubscript{2}, H\textsubscript{2}, H\textsubscript{2}O and CH\textsubscript{4} in high temperature oxygen sensor . The cross sensitivity investigations are carried out in the temperature range of 400\textdegree - 1100\textdegree C and reported that the reactive gases such as CO and CO\textsubscript{2} have only a reducing effect when present in concentrations of 1% in oxygen containing gas mixtures and remaining being N\textsubscript{2}. The H\textsubscript{2}, H\textsubscript{2}O, CH\textsubscript{4} shown reducing effect instead of oxidizing effect. They reported that the Strontium Titanate films are cross sensitive to above gases.

Mircea Anton and Beatrix Budy., (1994),[42] presented the influence of Rhodium (Rh) on SnO\textsubscript{2}-CO gas sensor. The sensing properties of SnO\textsubscript{2}-based elements to CO are markedly improved by the addition of a Rh catalyst. Rh loading modifies the surface properties and has non homogeneous structure. The sensors element is of
thick-film sintered type. The electrical resistance (R) of the sensors is measured at the end of the low-temperature period. They reported that the modification of the sensor surface to obtain a non-homogeneous structure is a powerful method to tailor the sensor-sensing performance as well as a reduced cross sensitivity.

I. Sayago et al., (1995), [43] investigated the effect of additives in tin oxide on the sensitivity and selectivity to NO, and CO. Undoped and Pt, In and Al doped film gas sensors are prepared by reactive sputtering. The selectivity of sensors was studied to determine the response of NO only when CO was the interfering gas. The concentration of CO is varied from 50-1000 ppm, NO from 2 to 70 ppm and temperature range of 300-675K. The best sensitivity to NO is achieved with sensor doped with Al or In and operated in the range of 300-500K. CO detection begins at 325K, with sensor doped with Pt. Further they reported that SnO sensors are sensitive to CO and NO.

S. Banno et al., (1995), [44] studied on nitrogen dioxide sensor based on nickel copper oxide mixed with rare earths. The films of oxide are prepared by an r.f. magnetron sputtering method and deposited on an alumina substrate and their NOx-sensing characteristics are studied. Thickness is estimated by the surface roughness meter. The crystallographic analyses of the samples are done by a fluorescent X-ray powder diffract meter. They reported that the sensors resistivity decreased with increasing the NO while it increases with NO. The resistance of the film changed more than that of the bulk, and it responded to the NO also.

P. Bogdanov et al., (1999), [45] describes the effect of nickel ions on sensitivity of In2O3 thin film sensors to NO2. Doping of In2O3 thin films with Ni2+ ions leads to the increase of their sensitivity to NO2. Sensitivity layers are usually prepared by means of different sputtering techniques. The response time of In2O3 sensors is independent on operating temperature. Recovery time significantly decreases when operating
temperature increases. Recovery time of In$_2$O$_3$-Ni$^{2+}$ sensors does not exceed 3 minutes at 250 $^\circ$C.

N.Bonini et al., (2000), [46] investigated the doping of a nanostructured titania thick films. The thick films of nano structured pure TiO$_2$, Nb/TiO$_2$, Ga/TiO$_2$ and Ti/TiO$_2$ are fabricated by screen printing technology. Structural, morphological and optical studies are reported to correlate the measurements to electrical performance. The films are characterised electrically in terms of conduction properties and grain to grain energy carriers. They reported that the firing temperature, grain size and dopent content strongly influence the gas response when the films are exposed to CO and NO$_2$.

Arturo Ortega et al., (2001), [47] carried out research work on intelligent detector based on temperature modulation of a gas sensor with a digital signal processor. The work is based on the device MiCS-1210P (CH$_4$,CO sensor from MicroChemical systems). The devices feature on a silicon micro machined substrate with an embedded heater and a SnO$_2$ thin film allowing quick changes in the working temperature heating frequency(60, 100 & 300mHz). They demonstrated the work in different temperatures modulation schemes, featuring extraction and classification algorithms and proposed the use of DSP as a core of detector to get rid of computational constraints required for some of complex algorithms that follow the dynamic processing to operate in real time. They proposed a system suitable for the implementation of the solution, minimizing the hardware to a single gas sensor and a DSP processor, and allowing the execution of proposed methods and more complex algorithms as a platform to test high performance set-ups.

J.Frank et al., (2001), [48] proposed a sensor system for indoor air monitoring using semiconducting metal oxides and IR-absorption system. A new sensor system
for a comprehensive indoor air monitoring is proposed which combines functionality of semiconducting metal oxides and infrared absorption for gas detection. The emission of infrared radiation by the heated metal oxide gas sensor and its propagation in the sensor system is modelled and experimentally validated. It is shown that even with the simple set-up of the system the infrared radiation can be used to detect indoor relevant CO₂ concentrations in the range of 1000 ppm with the IR system part. They reported that corresponding to the design and operation of the metal oxide gas sensor it detects explosive or toxic gas concentrations or volatile organic compounds in indoor applications.

S. Capone et al., (2001),[49] reported the development of an array of eight different micro sensors based on Pd doped SnO₂ nano crystalline sensing layers deposited by the sol-gel technology in the form of thick films on the top of Si-micro machine structures. The analyses of binary gas mixtures of CO and CH₄ in air at different relative humidity levels were investigated. PCA as pattern recognition (PARC) technique and PCR as multi variate analysis method have been applied to the input matrix that organizes in a vectorial way the response output of the sensors with the aim to identify and quantify the different binary mixtures. They reported that the PCR gave discrete results for the prediction of the real level of concentration of each component (CO and CH₄) in mixture, especially for medium high concentrations of two gases. They also proved the compatibility between the silicon micro machining technology for manufacturing micromachined substrates and the thick film technology, which produces high sensitive sensing elements.

Simone H. Hahn et al., (2001),[50] investigated on CO/CH₄ mixture measured with differently doped SnO₂ sensors. The discrimination performances of array consisting of differently Pd doped SnO₂ sensors operated at 350 and 400°C have been
investigated. The sensor signals are evaluated by using principle component analysis (PCA) and principle component regression methods. They reported that the array is able to discriminate between CO and CH₄ in varying relative humidity conditions.

P.Fau et al., (2001), [51] proposed nanosized tin oxide sensitive layer on a silicon platform for domestic gas applications. Micromachined silicon platforms have been specially created and are coated with a drop of tin oxide sensitive layer by a novel drop deposition technique. Tin dioxide powder, prepared by laser ablation, in suspension with water is dropped between electrical paths onto an alumina substrate. They reported that the sensors are highly sensitive to carbon monoxide and methane and are very stable to baseline resistance and gas sensitivity over time.

Th.Becker et al., (2001), [52] explained the gas sensing properties of thin and thick-film tin-oxide materials. Comparative gas sensing measurements have been performed on thin-film (50-300nm) and thick film (15-80µm) SnO₂ devices. Most of the commercially available gas sensors are based on thick-film metal oxide materials deposited on ceramic heater substrates. Diffusion reaction model is introduced in order to explain the measured differences between the thick and thin-film sensor responses. They reported that at normal sensor operation temperature of the order of 400°C thin film devices responded to oxidizing gases such as O₂ and NO₂ whereas thick film responded to reducing species like CO and CH₄, which shows that the tin oxide sensors are temperature dependent and also have cross sensitivity.

Ulrich Hoefer et al., (2001),[53] presented a comparison between a High temperature Ga₂O₃-gas sensors and SnO₂-gas sensors. Most of the commercial sensors are based on the SnO₂. In their work, comparison of the commercially available Ga₂O₃ and SnO₂ sensors concerning parameters like sensitivity, selectivity, long term stability, response and recovery time are investigated. Commercialized
STEINEL Ga$_2$O$_3$-sensors (SGAS2000, ethanol; SGAS2100, CO, CH$_4$) are compared with well introduced Figaro SnO$_2$-sensors (TGS 800 air quality, TGS 812 CO, propane, butane, TGS 842 CH$_4$) and results are presented. They reported that at high temp Ga$_2$O$_3$-gas sensors have been shown differences to other sensors based on the metal oxides like SnO$_2$.

J.F. Chang et al., (2002), [54] studied the effects of thickness and operation temperature on ZnO, Al thin film as CO sensor. Al- doped ZnO films are deposited onto SiO$_2$/Si substrates by rf magnetron sputtering system. The film thickness is varied by controlling the deposition time. The structure of deposition is determined by X-ray diffraction scanning electron microscopy and atomic force microscopy. They have shown that the films are flat and smooth. The CO gas sensing properties are determined by measurement of surface resistance of the thin film as a function of film thickness. They reported that the CO gas sensing properties are relative to the structural characteristics where the maximum sensitivity of 61.6% is obtained at 65nm film thickness at the operation temp of 400$^0$C.

K. Galatsis et al., (2002), [55] have investigated on the gas sensors for monitoring the vehicle cabin air quality by using metal oxide semi-conductors (MOS). Sensors fabricated with MoO$_3$ – TiO$_2$ and MoO$_3$-WO$_3$ thin films are investigated for comparing gas sensing qualities. They reported that the sensors are susceptible to poisoning in oxidising environment and sensitive to ambient temperature and humidity effects. The response of the sensor is 74% higher relative to the best commercial sensor tested.

G. Muller et al., (2003), [56] reported MEMS tool kit for metal-oxide-based sensing systems. They presented the components of MEMS toolkit and pointed out system functionalities that can be achieved by combining elements from this kit that largely
reduces heating power consumption. The various components of toolkit are explained. They reported that the silicon micromachining is used to reduce the heating power consumption and possibilities emerging in the field of metal oxide gas sensors using items from MEMS tool kit.

L. Francioso et al., (2003)[57] reported on the preparation and characterization of titanium dioxide thin film gas sensor devices for application in lambda measurement. The different responses for various concentrations of oxygen are analysed. The Ti2O units rely on the change of the semiconductor resistance with oxygen partial pressure. Using a software for simulating the composition of exhaust gases for different λ values, the sensors are exposed to complex exhaust mixtures, thus calibrating the sensor for the measurement of lambda.

Peter Tobias et al., (2003)[58] studied on interface states in high temperature gas sensors based on silicon carbide. Silicon carbide (SiC) based semiconductor devices are used for gas sensing in automotive exhausts and flue gases. The response of devices to reducing gases has been assumed to be due to a reduced metal work function at the metal oxide interface that shifts the flat band capacitance to lower voltages. They have also found that the high temperature (700K) exposure to hydrogen results not only in the flat band voltage occurring at the more negative bias than in oxygen, but also in the transition from accumulation (high capacitance) to inversion (low capacitance) occurring over a relatively narrow voltage range.

Rangachary Mukundan et al., (2003)[59] demonstrated a sensitive NOx sensor with a YSZ electrolyte and platinum & La1-xSrxCrO3 electrodes. The sensor has similar responses towards both NO and NO2, thus enabling it to be used as a total NOx sensor. They reported that HC and CO interference is negligible, and the PO2 and H2O content affect the sensor baseline.
Li Lin Li et al., (2005),[60] reported on platinum resistive film CO sensor without selective layer. Response in resistance of thin film sensors are studied in the presence of CO under constant operating current. Both oscillatory and non oscillatory changes in the resistance are examined. Experiments are carried in the CO concentration range from 50-1000 ppm at operating temperatures between 80-150°C. They reported that the amplitude and period increased with the increasing CO concentration. Further, in non oscillatory region, two different responses are observed, one of which the resistance of the sensor increased with increasing concentration and the other resistance decreased. It is believed that oscillations occurred between two branches of a Langmuir-Hinshelwood reaction mechanism. Above the upper branch of the oscillatory region, the resistance of the Pt films increases quasilinearly with increase of CO concentration and decreased below in the lower branch.

Manoj Kumar Ram et al., (2005),[61] proposed a CO gas sensor using the ultrathin nano-composite conducting polymer films. They have focused on the use of highly organized ultra thin conducting polymer/metal oxide (SnO$_2$, TiO$_2$) films for sensing of CO. The supramolecular approach has been utilized to fabricate films of conducting material (sulphonatedpolystyrene) via layer by layer (LBL) self assembly technique. UV-vis spectroscopy, atomic force microscopy (AFM) conductivity and AC impedance measurements are conducted to quantify the different characteristics of the ultra thin nanocomposite polymer films. They reported that nanocomposites supramolecular films are excellent for detection of CO gas.

S.M.A.Durrani et al., (2005),[62] investigated on CO-sensing property of undoped and doped tin oxide films prepared by electron beam evaporation. Undoped thin films of tinoxide and those doped with indium oxide and nickel oxides are deposited by electron beam evaporation. The effects of film thickness and preparation
conditions (films prepared with or without the presence of oxygen environment during deposition) on the optical and carbon monoxide sensing properties of the films are studied. The films are characterized by using X-ray diffraction and X-ray photo electron spectroscopy and optical spectroscopy techniques. All the films were found to be amorphous. It has been reported that the sensitivity of the films to CO increased with the thickness and porosity of the films. They reported that the selectivity to CO gas relative to CO$_2$ and SO$_2$ gases could be improved upon doping the films with indium (or nickel) oxide.

Youn-Ki Jun et al., (2005),[63] researched on the CO sensing performance in micro-arc oxidized TiO$_2$ films for air quality control mainly for automobile cabins. They reported that the obtained films exhibited maximum CO gas response at 350°C and the $R_d/R_g$ was ~ 1.6 for 10ppm CO. the sensor signal of the TiO$_2$ sensor is seen to be less susceptible to humidity exposure than the SnO$_2$-based sensor.

A. Fort et al., (2006),[64] reported about the CO sensing with commercially available SnO$_2$-based thick film sensors. They proposed a grey box model method for predicting the sensor response in presence of dry synthetic air and reducing gas CO during sensor temperature modulation. Three different commercially available Taguchi screen printed sensors are used (TGS2610, TGS2620 and TGS2442 Figaro engineering inc.). They reported that the model gave a good prediction of the sensors behaviour in the studied temperature range and when the temperature is lower than 250$^0$ C the sensor dynamics seems different which shows that the TGS sensors are temperature dependent.

A.M.Azad. (2006),[65] investigated on molybdenum oxide ceramic based chemical sensor for detection of CO via. microstructural modifications. They reported that, at a given temperature and standard pressure the oxidation of a metal to
its oxide or reduction of an oxide to metal or its sub oxides occurs at a well defined finite partial pressure of oxygen. MoO$_3$ thick film sensors fabricated from three different preparatory techniques are investigated. They proposed that the sensing mechanism and catalytic activity of ceramics are predominantly dependent on surface features in terms of small grain size, large surface area and porosity. MoO$_3$ films fabricated by regenerated oxide phase with unusual microstructure have shown a better gas sensing behaviour.

D. Koziej et al., (2006),[66] reported on CO sensing of undoped and Palladium doped Tin dioxide sensors derived from hydrothermally treated tin oxide. They reported that the impregnation of Pd results in increase of conductivity of tin oxide sensors in comparison to undoped sensors due to additional electrons provided by Pd.

E. Comini et al., (2006),[67] reported on influence of Iron addition in Tin oxide films prepared with RGTO (Rheotaxial growth and thermal oxidation) technique on ethanol and CO sensing properties. The Iron content was varied in the range 0-7%. The thin films are investigated by the volt-amperometric technique for gas-sensing properties. They reported that the layers are capable of sensing CO and ethanol and no evidence of surface poisoning is detected, and recovery of the resistance is complete and the response of the sensors is stable and reproducible at all operating temperatures tested during three months of operation.

Jean-Baptiste Sanchez et al., (2006),[68] developed a hybrid micro-system to get a sensitive and selective portable device for the detection of volatile organic compounds (VOC) in the air. Micro-Fabrication technology is applied for development of gas chromatographic micro-column. They reported that the prototype developed is small in size, great in chemical discrimination and fast in response.
K. Arshk et al., (2006),[69] studied on the development of array of polymer/MnO2/Fe2O3 mixtures in different percentages for use in gas sensing applications. Carbon black is added to each sample to improve base line resistance of the sensor and polyvinyl butyral as a binder. The thick film gas sensors are investigated by applying them onto the glass substrates with silver electrodes. They reported that, depending on the composition used the response of sensors to gas vapours has been changing. The selectivity of sensor to propanol was observed to increase with gas concentration with the maximum selectivity and incase of exposure to toluene the selectivity depended on the properties of sensing layer and gas concentration. Further, the sensor array showed a poor response to ethanol, chloroform and hexane at room temperature.

L. Malavasi et al., (2006),[70] investigated on materials development for CO-detection with improved selectivity through catalytic activation. Thin and thick films of NdCoO3, Nd0.8Sr0.2CoO3 and NiO-doped SiO2 are investigated. They reported that the cobaltates Sr-doped NdCoO3 showed an improved response with respect to pure NdCoO3 particularly at high temperatures and best results are obtained for thick films without the CoO layer at around 300°C. Nd0.8Sr0.2CoO3 sensing materials showed an easily measurable response upto 10ppm CO at 300°C. Thick films of Nd0.8Sr0.2CoO3 showed better response for high level of CO with respect to thin films which, on the contrary, are more effective in sensing low CO amounts. NiO nanocomposite films have shown a p-type response with high sensitivity to CO with optimal performance around 300 °C.

M. Kamionka et al., (2006),[71] have conducted experiments on calibration of a multivariate gas sensing device for atmospheric pollution measurement. In their study, they proposed two ways to calibrate a device (synthetic gas mixture and real
pollution) with three different screen-printed thick layers for the measurement of two components of the urban atmospheric pollution (Hydrocarbons and Nitrogen Oxides). The sensors were prepared by SnO$_2$ and are coated with Pt and SiO$_2$. The multisensory tests were done with synthetic gas mixtures composed of artificial air, ozone, unleaded petrol and nitrogen dioxide. The results are computed by measuring the change in resistance and change in conductance and analyzed the results using Neural Networks. In their results they represented that the problem of the measurement of pollution with semiconductor sensors is not easy because, the very low concentrations of pollutants need sensitive and stable devices.

P. Song et al., (2006),[72] studied on the structural, electrical and CO-sensing properties of La$_{0.8}$Pb$_{0.2}$Fe$_{1-x}$Co$_x$O$_3$. The La$_{0.8}$Pb$_{0.2}$Fe$_{1-x}$Co$_x$O$_3$ powders are prepared by citric method. They investigated on Co doping relationship with structural, electrical and CO sensing properties. The X-ray diffraction patterns showed that the La$_{0.8}$Pb$_{0.2}$Fe$_{1-x}$Co$_x$O$_3$ system formed a single phase only. They reported that cobalt content less than 0.4 showed the highest sensing response to CO gas.

Ren-Jang Wu et al., (2006),[73] studied the use of Cobalt oxide CoOOH in a carbon monoxide sensor operating at low temperatures. Cobalt oxide CoOOH is prepared from a Co(NO$_3$)$_2$ solution precipitation with NaOH and oxidation in air. The prepared samples are characterized by X-ray diffraction, temperature program reduction (TPR) and thermo-gravimetric/differential analysis (TG/DTA) techniques. The CoOOH is used as a sensing material on a semi conducting type CO sensor. They reported that the optimum CO detection working temperature is $80^\circ$C while the response time is 1 min. CoOOH has better response than Co$_3$O$_4$ and can detect CO concentrations of 1ppm.
S.Ajami et al., (2006),[74] reported on the highly selective sensor to CH₄ in presence of CO and ethanol using LaCoO₃ perovskite filter on Pt/SnO₂. LaCoO₃ perovskite was used as an active filter to suppress the sensitivity of a Pt/SnO₂ sensor to CO and C₂H₅OH. They reported that the Pt/SnO₂ gas sensors are highly sensitive to ethanol and CO but using LaCoO₃ perovskite as active filter eliminates sensitivity of the sensor to CO and ethanol and increases its selectivity to methane.

S. Capone et al., (2006),[75] investigated on the influence of electrodes (Ti-Au) ageing on the properties of doped and undoped micro sensors, based on tin oxide prepared by the sol-gel deposition technique. The influence of the ageing of the Ti/Au interdigitated electrical contacts on the response of the samples has been investigated. They reported that the main disadvantage of the metal oxide based sensor is a gradual loss of stability & reliability, namely the problems of ageing and drifting the sensors sensitivity.

Shurong Wang et al., (2006),[76] investigated on Tin dioxide nanocrystals by a precipitation process and used as the support for 2wt.%gold/tin dioxide preparation via a deposition-precipitation method, followed by calcinations at 200 °C as low temperature CO gas sensor. Thick films are fabricated from gold/tin dioxide powders, and the sensing behaviour for CO gas is investigated. The Au/SnO₂ calcined at 300 °C exhibited better CO gas-sensing behaviour than the SnO₂ calcined at other temperatures. They reported that the experimental results indicated the potential use of Au doped SnO₂ for CO gas sensing. They observed that the gold/tin dioxide is found to be efficient CO gas sensing materials under low operating temperature.

S.M.A. Durrani (2006),[77] investigated the influence of electrode metals and its configuration on the response of tin oxide thin film CO sensor. The electrode materials used are Ag, Al, Au and Pt along with different electrode configurations. Pt
and Au electrodes showed higher response than Ag and Al electrodes. He reported that the CO sensing properties depends both on electrode material and configuration.

A. Chaiyboun et al., (2007),[78] proposed a logarithmic multi-parameter model for main and cross sensitivities to estimate gas concentrations in a gas mixture for SnO$_2$ gas sensors. They have developed a sensor response equation using simple logarithmic model with two coefficients. These coefficients changes with the type of sensor material, the type of reducing gas and the temperature of the sensor. The characteristics of two mixture gases methane and hydrogen, methane and carbon monoxide are investigated. They expressed that the model is not suitable for very low concentration of the gases.

G. Korotcenkov et al., (2007),[79] investigated on the influence of additives on gas sensing and structural properties of In$_2$O$_3$-based ceramic sensors. They studied on Raman’s scattering spectra of In$_2$O$_3$–doped ceramics such as Cu, Mn, Ga and Se. They reported that there is no universal law describing the influence of doping on gas sensing properties of metal oxide sensors. Each dopant has its own specificity, depending on the type of introduced impurity and its concentration.

S. Radhakrishnan and Santhosh Paul., (2007),[80] investigated on polypyrrole modified with ferocene (Fc) with direct incorporation during polymerization so as to increase its sensitivity for carbon monoxide gas sensor applications. Synthesis is carried out by chemical oxidative polymerization in the presence of ferrocene using ferric chloride. The CO response measurement is carried out for the sensor fabricated in a surface cell model. They reported that the sensor response and recovery is very fast and depends on the film composition. The response factor is found to be maximum for 1.32mol% Fc content in the polymer.
S.M.A. Durrani et al., (2007),[81] investigated on CO-sensing properties of hafnium oxide thin films prepared by electron beam evaporation. The effects of the film thickness and preparation conditions on the optical and CO sensing properties are studied. The films are characterized by X-Ray diffraction and X-Ray photo electron spectroscopy. He reported that films deposited on unheated substance are amorphous, where as those deposited on heated substance showed a mixture of amorphous and polycrystalline structure. Further, the sensitivity of the film to CO increased with the thickness and the porosity.

A. Tischner et al., (2008),[82] investigated on nano crystalline SnO$_2$ ultra thin film gas sensors fabricated by spray pyrolysis for the detection of humidity and carbon monoxide. The structure of SnO$_2$-layers has been characterized by SEM, AFM, and XPS analysis. They reported that the sensors have high sensitivity when operated at $250^0-400^0$C with thickness of 50 to 100nm and can be able to detect CO concentration less than 5 ppm. The spray pyrolysis process offers a comparable way to modify chemical composition of SnO$_2$ layers by dopants like In and Sb.

G. Neri et al., (2008),[83] investigated on pure and Sn-doped In$_2$O$_3$ nanopowders in the monitoring of CO for automotive applications. They reported that the Sn-doped In$_2$O$_3$-based sensor showed higher conductance than In$_2$O$_3$, due to n-doping of Sn cations in the In$_2$O$_3$ lattice, and higher defectiveness than pure oxide and the sensor showed high response to CO. The undoped In$_2$O$_3$ sensor showed the best performances in terms of sensitivity, response/recovery time and lower detection limit.

S.M.A. Durrani et al., (2008),[84] reported on Carbon monoxide gas sensing properties of cerium oxide thin films prepared by electron beam deposition. The thin films of cerium oxide are deposited by e-beam evaporation on unheated substrates.
They were characterized by using X-ray diffraction, AFM and optical spectrophotometry and found to be amorphous and highly porous. They reported that the films are highly sensitive to CO and the response magnitude strongly depends on bias voltage, gas concentration and operating temperature. The lower detection limit is 500ppm, optimum operating temperature 390°C and response and recovery times are 45 s and 25 s respectively.

S. Wang et al., (2008),[85] reported on dc and ac response of SnO$_2$ sensor to CO. SnO$_2$ sensor response on CO is detected by dc potential and ac impedance methods. They reported that the sensor response increases with increase in temperature and more at 623°C. The maximum response is observed at CO concentrations of 500 to 1500 ppm and the ac impedance method is promising to detect CO with the SnO$_2$ sensor. Further they reported that the SnO$_2$ sensors are temperature dependent.

X. Du and S.M. George, (2008),[86] reported on the sensor response for CO gas sensing by tin oxide film and its dependence on thickness grown using atomic layer deposition technique(ALD). The tin oxide films are deposited on flat templates using atomic layer deposition techniques with SnCl$_4$. They reported that the maximum sensor response for CO gas sensing is observed at a SnO$_x$ ALD film thickness of 26.2Å and high response at temp 250°C and 325°C which reports that tinoxide film sensors are temperature and thickness dependent.

Arthur Valleron et al., (2009),[87] investigated the possibilities of semi-conductor gas sensor for automotive application. The sensing element is tin dioxide layer with gold electrodes. They investigated on both oxidising and reducing gases in the range of 250°C-600 °C. They reported that the sensor detects NO at low temperature 350°C-400 °C, which exceeding 500 °C detects CO.
Noriya Izu et. al, (2009), investigated on CO sensors using cerium oxide thick films with various particle sizes and Pt/alumina as catalyst. They reported that TF950-NO (Thick film sintered at 950 °C with no catalyst) with a particle size of 50nm displayed a better gas response and lower resistance than TF800-NO and TF1000-NO and the resistance of TF950-NO changed more quickly than that of TF800-NO and TF1030-NO when air including CO is introduced and the response time of TF950-NO is approximately 2s and the connected sensor element using TF950 and the Pt/alumina catalyst(CS-TF950) showed a low response to combustible gases such as methane, ethane, propane, and H₂ at 450 °C.

Ren-Jang Wu and Wei-Chen Chang et al (2009), prepared various ratios of CoOOH-WO₃ sensing materials from CoOOH and tungsten. Au and single wall carbon nanotube(SWCNT) are also added to CoOOH-WO₃ materials to detect CO concentration. The resulting CoOOH-WO₃ material is used as a semi conductor p-type CO sensor. The mixture with a CoOOH-WO₃ ratio of 2:1 had the highest sensor response and the sensor head worked at room temperature. A mechanism of CO sensing is proposed based on the adsorption and desorption processes of CO and surface oxidation reactions. The addition of SWCNT and Au can increase the number of CO adsorption sites and enhance the sensor response.

Tong Zhang et al., (2009), investigated on In/Pd doped SnO₂ via a sol-gel method and coated on a silicon substrate with Pt electrodes to fabricate a microstructure sensor. They reported that the sensor has high response to CO with very low cross response to common interference gases at an operating temperature of 140 °C.
2.4 MEMS Based Sensors

J.C. Belmonte et al., (2006),[91] investigated on micro machined twin gas sensor for detection of CO and O\textsubscript{2} on catalytically modified nano-SnO\textsubscript{2}. The two gases CO and O\textsubscript{2} have high sensitivity to SnO\textsubscript{2}. The SnO\textsubscript{2} nano particles of both sensors are catalytically modified with different Pd loadings that act as active filters so as to convert one sensor highly response sensitive to CO than O\textsubscript{2}. They reported that the behavior of the sensor for different oxygen concentrations is almost the same for both sensors while the sensor with low palladium loading is highly sensitive to CO and with high palladium loading sensor is not very sensitive to CO.

M. Graf et al., (2006),[92] presented on monolithic gas sensor microsystem fabricated in industrial CMOS-technology combined with post-CMOS micromachining using nano crystalline Pd doped SnO\textsubscript{2} thick film as the sensitive material. They designed a new type of micro hotplate on-chip circuitry for operating temperature up to 500\textdegree C. They reported that the sensor is able to detect concentration of CO up to 1ppm.

L. Francioso et al., (2008),[93] investigated on a linear temperature microhotplate gas sensor array for automotive cabin air quality monitoring. Using the simultaneous outputs from eight different signals coming from a WO\textsubscript{3} thin film structure heated in a linear temperature gradient mode, the evaluation of gas sensing properties of metal oxide materials, typically around 300 to 400\textdegree C are studied. Three different gases of CO, NO\textsubscript{2}, and SO\textsubscript{2} at different concentrations are analysed. The capability of the array to act as a single die miniaturized electronic nose has been validated by the gas sensing test.
Q. Tang et al., (2008),[94] explained the preparation of gas sensors via dip-pen nanolithography. Conducting polymer and doped polypyrrole are used to develop a gas sensor by dip-pen nanolithography (DPN). The response time of sensor to 18ppm CO\textsubscript{2} is 9s. The sensor response increased linearly as the CO\textsubscript{2} concentration increased. They reported that the sensor is suitable for sensing CO\textsubscript{2} at ppm resolution.

Tian. Xu et al., (2008),[95] proposed a thermoelectric(TE) carbon monoxide sensor using Co-Ce as catalyst. Bismuth telluride is chosen as the TE material for remarkable Seebeck effect. The CO sensor was prepared by employing a TE thin film (Bi-Te PN) and Co-Ce Oxide. The TE layer was deposited onto a quartz glass substrate by magnetron sputtering with Co-Ce oxide centred in the TE layer. They investigated on effect of atomic ratio of Co/Ce, pH value, tablet compression pressure, and catalyst temperature. They reported that the optimal values of the sensor preparation are 7.1 pH value, 1 MPa tablet pressure, catalytic Co\textsubscript{10}Ce at an operating temperature of 92 °C and response and recovery times as 72s and 68s.

Yoon-Sung Kim et. al, (2008),[96] proposed CuO nanowire gas sensor for air quality control in automotive cabin. The CuO NWs are prepared by thermal oxidation which exhibit higher crystallinity and longer aspect ratios compared to those prepared via solution based routes. They reported that the sensor resistance increased at high NO\textsubscript{2} concentrations (30-100ppm) but decreased with decreasing NO\textsubscript{2} concentrations down to less than 5ppm and increased upon exposure to 10-100ppm CO which shows the NO\textsubscript{2} sensing characteristics got varied according to the NO\textsubscript{2} concentrations.

Anton Kock et al., (2009),[97] reported a new approach for the fabrication of ultra-long single crystalline SnO\textsubscript{2}-nanowires for gas sensing applications based on a combined spray pyrolysis and annealing process. The SnO\textsubscript{2}-nanowires are developed on SiO\textsubscript{2}-coated Si-substrates. The whole SnO\textsubscript{2}-nanowire fabrication procedure is
performed at atmospheric pressure and requires no vacuum. They reported that the evaporation and condensation process converts the nanocrystalline SnO\textsubscript{2}-films into single crystalline SnO\textsubscript{2}-nanowires directly on the chip. Evaporation of Ti/Au contact pads on both ends of single SnO\textsubscript{2}-nanowires enable their direct use as sensing elements.

All the above works are related to gas sensors for various applications such as detecting CO, CO\textsubscript{2}, NO, NH\textsubscript{3} etc. Most of the research reports expressed that sensors sensitivity and selectivity depends on the various factors such as geometrical orientation, shape, thickness, operating temperature etc. It is noted from the literature that there are some works available in medical field for sensing the biological analyte using microcantilever biosensors.

Some of the microcantilever based biosensors and chemical sensors are discussed in the present review of literature.

2.5 Micro Cantilever Based Chemical Biosensors

T.Thundat et al., (1995),[98] investigated on changes in the resonance frequency of microcantilevers due to adsorption of analyte vapour on exposed surfaces. Frequency changes may be due to mass loading. Cantilevers coated with a thi gelatin film exhibit high sensitivity and a linear response with changes in relative humidity. Static cantilever deflection also changes with vapor adsorption. Both phenomena can be used to detect adsorbed vapours with pictogram mass resolution. They reported that, if an array of cantilevers are used with a variety of coatings, specific chemical fingerprinting of mixed or unknown analytes recognition is possible based on pattern recognition from the differential response of the individual cantilevers.
G.Y.Chen et al., (1995),[99] have investigated that the resonance frequency of a cantilever can change due to a combination of mass loading and change of spring constant resulting from adsorption of chemicals on the surface. Cantilevers also undergo static bending that is induced by differential surface stress. They reported that the magnitude of these effects depends on the chemical properties of the surface and also on the amount of material adsorbed. Hence, cantilever deflection as well as resonance frequency change can be used as the basis for the development of chemical sensors.

H.P.Lang et al., (1999),[100] presented a novel chemical sensor based on a micromechanical array of silicon cantilevers. Chemical reactions are transduced by serialization of cantilevers with coatings such as metals, self-assembled monolayers, or polymers into a mechanical response. The optical beam-deflection technique is used as readout scheme. Coating of each cantilever sensor with a different sensitive layer allows operation of the array-device as a new form of chemical nose. Detection of hydrogen, primary alcohols, natural flavours, and water vapour is demonstrated by them. They reported that the magnitude of sensor response is proportional to the amount of analyte present.

A.Biosen et al., (2000),[101] developed an AFM probe with integrated piezoresistive read-out and applied as a cantilever-based environmental sensor. The probe has a built-in reference cantilever, which makes it possible to subtract background drift directly in the measurement. The integrated read-out facilitates measurements conducted in liquids. The probe has been successfully implemented in gaseous as well as liquid experiments. They reported that the sensor can be applied as a laser power meter and as a humidity sensor.
A.M.Moulin et al., (2000),[102] investigated the use of surface stress-based sensors as bio-chemical sensors. In principle, adsorption of bio-chemical species on a functionlized surface of a microfabricated cantilever causes surface stress and consequently the cantilever bends. Two applications are presented: first lipoproteins and their oxidized form which are responsible for cholesterol accumulation in arteries are differentiated by measuring the surface stress involved in their adsorption on sugar; secondly, the surface stress resulting from surface induced conformational changes in protein is monitored. The possibility of detecting the difference between LDL and oxLDL with surface stress method is demonstrated. There are significant problems in the interpretation of the underlying cause of surface stress when the adsorbents are large, molecularly complex and electrically charged. They reported that the detailed research is required to know the utility of this technique as a useful diagnostic biosensor.

Henriette Jensenius et al., (2000),[103] investigated on a developed microcantilever probe with integrated piezoresistive read-out as a gas sensor. Resistors sensitive to stress change are integrated on the flexible cantilevers. A polymer coated cantilever has been exposed to vapours of various alcohols and the response has been interpreted using a simple evaporation model which is a direct measure of the molecular concentration of alcohol vapour. On the basis of the model, the detection limit is determined to be below 10ppm for alcohol vapour measurements. They reported that the time response of the cantilevers can be used to distinguish between different alcohols due to a difference in the evaporation rates.

M.K.Baller et al., (2000),[104] presented quantitative and qualitative detection of analyte vapours using microfabricated silicon cantilever array. During exposure to the analyte, the swelling of polymer layer on the cantilever is monitored and the
transduction of physical and chemical processes into nanochemical motion of the cantilever is observed. This motion is tracked by a beam-deflection technique using a time multiplexing scheme. The response pattern of eight cantilevers is analysed via principle component analysis (PCA) and artificial neural network (ANN) techniques. They reported that the sensor can be employed to create fingerprints of analytes which facilitate the application of the device as an artificial chemical nose. Its major advantages are the capability to use reference sensors for differential measurement that compensate for superimposed disturbances.

F.M.Battiston et al., (2001),[105] presented a chemical sensor based on a microfabricated array of eight silicon cantilevers actuated at their resonance-frequency and functionalized by polymer coatings. The operating principle is transduction of chemical or physical processes into a mechanical response. They reported that the cantilever bending and resonance-frequency shift during exposure to analyte vapour and it can be used for qualitative, quantitative characterization and recognition of a variety of chemical substances. Application areas of such sensors are mainly in quality and process control.

Roberto Raiteri et al., (2001),[106] investigated on the merging of silicon microfabrication techniques with surface functionalization. Biochemistry offers new and exciting opportunities in developing microscopic biomedical analysis devices with unique characteristics. Microcantilevers can transduce a chemical signal into a mechanical motion with high sensitivity. Cantilever based sensors are extremely versatile. They can be operated in air, vacuum and liquid environment. They also discussed the advantages of this novel technique as well as its potentials.

Samuel Kassegne et al., (2001),[107] investigated on the mechanical design and optimization of high-sensitivity piezoresistive cantilevers used for detecting changes
in surface stress due to binding and hybridization of biomolecules on the surface of the cantilevers. They presented several design solutions in optimizing the cantilever mechanical design to address the sensitivity required when approaching recognition of single base pairing of DNA molecules. The sensitivity of piezoresistive cantilevers depends on the depth of the piezolayer and its doping characteristics. It is often an expensive exercise to determine the optimum design parameters for increased sensitivity. They reported that the “managed solution” based on a finite element simulation is used to help in determining optimum location and depth of piezoresistive layer. The use of a finite element method based simulation to arrive at optimally located piezoresistive layer is demonstrated.

D.R. Baselt et al., (2002),[108] presented the design and the effects of basic environmental parameters on a micro electro chemical hydrogen sensor (MEMS) which contains an array of 10 micromachined cantilever beams. Each cantilever is 500µm X 267 µm X 2 µm thick and has a capacitance read-out capable of measuring cantilever deflection within 1nm. They reported that the response magnitude decreases with increasing temperature, humidity and oxygen concentration. The sensor can detect hydrogen concentrations between 0.1 to 100% with roughly linear response between 10 and 90% hydrogen. The 0-90% response time of a unheated cantilever to 1% hydrogen in absence of air is about 90 s at 25 °C and 0% humidity.

J.J. Headrick et al., (2002),[109] reported that the use of chemically selective thin-film coatings have shown to enhance the chemical sensitivity of MicroCantilever (MC) chemical sensors. Structural modification of Micro Cantilever chemical sensors can improve the stress transduction between the chemical coating with MC. Sub-Micron channels are milled across the width of the MC. Responses of the nanostructured and coated MC’s to 2,3-dihydroxynaphthalene and a series of volatile
organic compounds are reported. A comparison is made with the previously reported method and showed an increased sensitivity of these devices as chemical sensors. This increase in sensitivity is produced by improvement of the transduction of stress created in a chemical receptor phase, by analyte adsorption to surface stress which results in larger deflections of MC tip. They reported that the future optimization of MC chemical sensors will involve increasing the thickness of coatings and investigating further the effects of groove size, density and thinner cantilevers.

Mar Alvarez et al., (2002),[110] developed a novel technique for detection of the organochlorine insecticide compound dichlorophenyltrichloroethane (DDT) by measuring in nanometer scale through bending of a micro cantilever produced by differential surface stress. The immobilization process is characterized by monitoring the cantilever deflection in real time. Thus specific detection is achieved by exposing the cantilever to the sensitized biosensor with nanomolar sensitivity. They presented a novel technique for immunodetection of pesticides by measuring the nano mechanical response of the micro cantilever. They reported that the Nanaomechanical biosensors are more sensitive devices for pesticide detection using immune reactions area compared with the other label-free sensors such as the surface Plasmon resistance biosensor and the quartz crystal micro balance.

Isabelle Dufour and Ludivine Fadel (2003),[111] reported that silicon microcantilevers can be used as microbalances or chemical microsensors if a sensitive layer is deposited on moving structures. They presented analytical expressions for the sensitiveness of different structures obtained in view of optimization of the geometrical parameters for both mass sensors or concentration gas sensors. They reported that for chemical sensors, a thin parallely piped microcantilevers with sensitive coating on the whole surface gives good performance and for frequency
measurement the active surface can be improved with a rectangular plate at the free-end.

Matthew Hopcroft et al., (2003),[112] reported that SU-8 is a photo plastic polymer with a wide range of applications in micro technology. Cantilevers designed for a commercial atomic force microscope are fabricated with SU-8. The mechanical properties of these cantilevers are investigated using two micro scale mechanical testing techniques such as contact surface profilometer deflection known as MAT-test and static load deflection using a specially designed test machine, the MFT2000, a versatile instrument used to perform a wide variety of mechanical tests on a micro scale samples.

Chatzandroulis et al., (2004),[113] fabricated a capacitive type chemical sensor based on silicon /polymer bimorph structure. Polymer covering the thin silicon membrane swells inducing a deflection on the membrane which is measured as a capacitance change between membrane and substrate upon exposure to analyte. Five different polymer layers are examined. They reported that the differences in the sensitivities between these layers may be exploited in constructing an effective chemical discriminating array. Exposure to water, methanol and ethanol vapours is used to evaluate performance.

L.A. Pinnaduwage et al., (2004),[114] reported on the gas phase detection of 2,4-dinitrotoluene (DNT) with a SXFA-[poly(1-(4-hydroxy-4-trifluormethyl-5,5,5-trifluoro)pent-1-enyl)methylsiloxane]-polymer –coated microcantilevers. The response is reversible and the sensor coating has shown its ability to withstand repeated exposure to varying levels of DNT concentrations over a year. The 2,4-DNT can be detected of their sensitivity at 300 parts per trillion (ppt) levels within a few seconds, They reported that, high sensitivity, rapid and reversible detection, together
with the micrometer-size of the cantilever can be expected to lead to a portable detection device that can be used for rapid and sensitive detection of explosion vapours.

D. Then et.al., (2006),[115] developed a highly sensitive self-oscillating cantilever array for the quantitative and qualitative analysis of organic vapor mixtures. The cantilevers are driven by an electrostatic and magnetic actuation which is developed with a closed feed-back loop which forces the cantilever to oscillate always at its resonance frequency. Polymer coatings are used to detect specific chemical interactions. They reported that by calibrating the system, it is possible to predict the composition as well as the concentration of unknown gas mixtures.

L. Gammelgaard, et al., (2006),[116] presented an SU-8 micrometer sized cantilever strain sensor with an integrated piezoresistor made of a conductive composite of SU-8 polymer and carbon black particles. The composite has been developed using ultrasonic mixing. The composite material has been integrated into an SU-8. Since SU-8 is much softer then silicon and the gauge factor of the composite material is relatively high, this polymer based strain sensor is more sensitive than similar silicon based cantilever sensor.

L.G. Casrroscosa et al,(2006),[117] presented a review on Nanochemical biosensors. The review covers the basic working principles, types of sensor formats, fabrication, reported applications in chemical and biological analysis, trends in cantilever fabrication, examples of commercial instruments available and future developments. They reported that biosensors based on microcantilevers have become a promising tool for directly detecting biomolecular interaction with great accuracy.
Arnab Choudhury et al., (2007),[118] presented a procedure for the fabrication of a piezoresistive microcantilever array for surface-stress based chemical and biochemical sensing applications. They used a n-doped silicon piezoresistors which are more advantageous than the usual p-doped piezoresistors. They presented a model for cantilever deflection that allows for the estimation of the surface stress response during analyte measurement and the cantilever curvature caused by the residual stresses in the structural layers.

C.Drake et al., (2007),[119] reviewed metallic nanostuctured materials based sensors. The review covers gas sensors, volatile organic compound sensors, biosensors and sensing mechanisms, principles, merits and demerits along with some of the applications. Further, the review encompasses some significant efforts on the applications of nanomaterials in the various sensing systems.

Chengyin Wang et al., (2007),[120] discussed the developments and the principles of cantilever based sensors and their versatility. Cantilever based sensors can transduce a number of different signals into a mechanical response detectable by various methods and they can be used in air, vacuum or liquid environments. They reported that the sensors based on cantilevers have the focus of attention in biomedicine and chemistry, where they offer advantages in sensitivity, time response, analysis time, fabrication cost, miniaturization and potential for large sensor array.

Sandeep Kumar Vashist, (2007),[121] reviewed the usage of microcantilevers for sensing applications. The major advantages include high sensitivity, low cost, low analyte requirement. He also reviewed a major breakthrough in sensors, i.e. the development of nanocantilevers.
Timothy L. Porter et al (2007),[122] developed a solid-state sensor platform for the detection of hydrogen cyanide gas. They found that using a keratin matrix functionalized with thiolated gold nano-particles as a sensing material, embedded piezoresistive microcantilever sensors showed a fast response to levels of HCN gas that may be lethal to humans.

A. Loui, F.T. Goericke et al., (2008),[123] investigated the effect of piezoresistive microcantilever geometry on cantilever sensitivity during surface stress chemical sensing. They reported that high aspect ratio cantilevers are optimal for point-loading applications and low aspect ratio cantilevers that are short and wide are optimal for surface stress-loading situations, such as in biological and chemical sensor applications.

Eric Finst et al., (2008),[124] investigated on the geometric and environmental effects on cantilever measurements including the chemical nature of the underlying interactions. To address the geometric effects they have considered cantilevers with rectangular or circular cross-sections. The chemical nature is addressed by using cantilevers fabricated with metals and/or dielectrics. Selective chemical etching, swelling or change in Young’s modulus of the surface is investigated by means of polymeric and inorganic coatings. They reported that the cantilevers provide genuine tools for the investigation of the mechanical properties of small volume of materials and their temporal evolution under gaseous environment.

Jonan Flueckiger et al., (2009),[125] have studied microfabricated formaldehyde gas sensors. Sustained exposure to low levels of formaldehyde can lead to adverse health effects. They reviewed microfabricated devices such as microhotplates for metal oxide sensors, enzyme-based electrochemical sensors and nanowire based sensors. They investigated on polymer based sensor in detection of Formaldehyde.
They reported that the polymer and polymer composite sensor materials have the potential to offer advantages, at room temperature operation with increased sensitivity and selectivity.

Ying Chen et al., (2010),[126] reported on bio/chemical detection in liquids with self-sensing Pr-Oxi lever (piezo-resistive SiO$_2$ cantilever) sensors. Advantages of microfabrication technologies have triggered new applications for microtools. They developed silicon piezoresistance encapsulated SiO$_2$ cantilever (Pr-Oxi lever) with the electrical interconnection wires insulated by SU-8 coating functionalized with siloxane-based molecular layer. They reported that the sensor is successfully used in detection of 2.5% aqueous tetramethyl ammonium hydroxide (TMAH) and avidin at $10^{-1}$ mol/ml trace level.

Sandeep Surya et al., (2011),[127] reported on functionalized piezoresistive nanoelectromechanical cantilevers as promising tools for sensor applications. This paper reports on integration of fabricated piezoresistive cantilever sensors and sensitive analog front end circuit for detection of bio-markers. The system operates on the principles of nanometer deflection of cantilever sensors, due to antigen-antibody interactions. A wheatstone bridge connected resistors has been used where the functionalized cantilever forms one of the arms. The measured results are presented along with calibration technique. They reported that the system may be used for a variety of other applications, such as, explosive detectors and gas sensors.

The above works are based on optical, deflection, frequency and mass change of the cantilevers in the biosensors.

A few reports available on sensors functionalized with porphyrins are presented below.
2.5.1 Sensors using Porphyrins

D.-G. Zhu et al., (1992), [128] have investigated on Langmuir-blodgett film formation and properties of a Ruthenium porphyrin complex in sensing of nitrogen dioxide. Ellipsometry reveals the thickness per layer to be 1.65+0.05 nm. A marked increase in the in-plane electrical conductivity of these layers is found upon exposure to nitrogen dioxide. This effect is found to be reversible at room temperature. As reported on the monolayer formation and LB film fabrication of a ruthenium porphyrin complex, the LB layers are found to exhibit semiconducting electrical behaviour with a thermal activation energy for conduction between 20 to 100 °C.

C. Bernard et al., (1998), [129] reported on the electrochemical behaviour of iron porphycenes in benzonitrile, tetrahydrofuran, N,N-dimethylformamide, and dichloromethane in the presence of Lewis bases. The analysis combined the use of polarographic, steady-state voltammetric, cyclic voltammetric, and spectroelectrochemical methods. Iron(III)2,7,12,17-tetra-n-propylporphycene ([Fe\textsuperscript{III}TPrPn]Cl) is reduced in three one-electron steps and is oxidized in two one-electron steps: They reported that in the presence of CO, the reduction of iron(III) generates ([Fe\textsuperscript{II}TPrPn]Cl).

Roberto paolesse et al., (1998), [130] investigated the Self assembled monolayers of mercaptoporphyrins as sensing material for quartz crystal microbalance chemical sensors. Thiol-functionalized metalloporphyrin (Cobalt and Manganese) have been deposited as self-assembled monolayers onto the gold pad of quartz crystal microbalances (QMBs). The self assembled mono layers are prepared by immersing the sensor in dichloromethane of the metalloporphyrin for 24 hrs. They expressed that
the deposition of monolayers of thiol-functionalized metalloporphyrins is a useful approach to develop QMB sensors for VOC detection. Further they have reported that the functionalized QMB allowed the detection of species such as Benzene and other Hydrocarbons that are impossible with cast-coated sensors.

Arnaldo D’Amico et al., (2000),[131] describes the mettaloporphyrins as basic material for volatile sensitive sensors. Deposition techniques and possible transduction mechanisms are reviewed. This feature makes porphyrins eligible as good sensing material able to detect the volatile organic compound (VOC) present in the environment. The results show that the presence of peripheral substituents may increase or decrease the cofacial orientation of the molecules. They reported that these transductions mechanisms once optimized, could suggest the best system to be utilized in the modern versions.

Corrado Di Natale et al., (2000),[132] studied on the sensitivity variations induced by modification of the basic porphyrins, used as coatings on QMB sensors. Special attention is paid on the influence of coordinated metal and the peripheral substituent on the selectivity properties of metalloporphyrins. Two sets of metalloporphyrins have been prepared and tested. They reported that the metal coordinated to TPP strongly influence sensitivity pattern of the sensor. When the VOC molecules contain a donor atom, such as oxygen or nitrogen, the most important effect of the central metal can be directly related to the coordinated interactions between the VOC and the metal centre.

C.Di Natale et al (2003),[133] investigated on the metalloporphyrins based sensors to measure the biological damage of carbon monoxide exposure. They reported that the oxygen transport in blood is threatened by the presence of CO as it permanently replaces the oxygen molecule in the haemoglobin making this ineffective as oxygen
carrier. This mechanism is ruled by the properties of a particular metalloporphyrin (heme) for which the binding energy with CO is about 250 times higher than that towards oxygen. In this paper a sensor system based on the properties of metalloporphyrins with a calorimetric read-out is illustrated. This system is sensitive both to the concentration of CO and to the exposure time. Results shown a good accuracy of the carboxy-haemoglobin(HbCo)percentage.

O.M.Guimaraes et al., (2006),[134] developed a system where carbon monoxide is detected and determined by a piezoelectric quartz crystal sensor coated with nickel(II)-phthalocyanine. Studies on the effect of temperature, flow rate are carried out. Calibration curves, sensor stability and precision of measurements are also verified. It is observed that the interaction between CO and NiPc increases at higher temperatures. They reported that the advantage of chemical immobilization is possible to shorten the response time due to the lower influence of diffusion phenomena on the film surface.

B.Wang et al., (2007),[135] studied on preparation, characterization and gas sensing properties of lead tetra-(tert-buty-tetraazaporphyl)-5, 10, 15, 20-tetraazaporphyrin spin-coated films. PbTAP(t-Bu)₄ is obtained and characterized by IR spectra, absorption spectra and atomic force microscopy. The response and recovery characteristics of the films to NH₃, NO₂, and C₂H₅OH vapours are investigated at room temperature. Further, reversibility and stability of the films to NH₃ are also presented. They reported that the sensor fabricated with spin coated films of PbTAP (t-Bu)₄ has good response, short response time and stability when exposed to NH₃ in the range of 4-40ppm at room temperature. The UV-Vis absorption spectra, IR spectra and AFM images indicated that the films presented a disorderly, aggregated and perforated macrostructure, enhancing the sensing property.
M. Tonezzer et al., (2007), [136] reported on optical sensing properties of CoTPP thin films deposited by glow-discharge-induced sublimation in detection of ethanol vapour. Thin porphyrin assemblies used as gas sensing materials are usually produced through chemical deposition techniques. In this work a new physical technique named glow-discharge-induced sublimation (GDS) has been employed for the production of Cobalt 5,10,15,20 meso tetraphenylprophyrin (CoTPP). For comparison films are also produced by vacuum deposition and spin-coated techniques. They reported that the optical measurements performed in ethanol-vapour–containing nitrogen flux highlighted that the response of GDS films are one order of magnitude more intense than those of the films deposited through spin coating and vacuum evaporation techniques. Further, the inspection of the surface morphology with scanning electron microscope evidenced the very high surface roughness of the GDS samples.

Karim Salazar et al., (2009), [137] modelled a sensor based on the porphyrin nucleus of the soluble guanylate cyclase enzyme and tested with nitric oxide and carbon monoxide. Molecular oxygen is tested as a possible interferer. Geometries and electronic structures of the model are assessed by density functional theory. Vibrational circular dichroism (VCD) infrared and raman spectra are obtained for iron complexes. The gas detection is obtained by electrical signals and complemented with spectroscopic techniques. They reported that the pollutants may be detected and measured with the proposed biosensor.

Muhammad Saleem et al., (2009), [138] investigated on Cu(II)5,10,15,20-tetrakis(4-isopropylphenyl)porphyrin based surface type resistive-capacitive multifunctional sensor. CuTPP is synthesized and deposited as thin film by thermal evaporation on a glass substrate with preliminary deposited silver electrode and Ag/CuTPP/Ag surface type multifunctional sensor. They reported that the change in electrical resistance and
capacitance is observed with increase of temperature, relative humidity and illumination.

Necmettin Kilinc et al., (2009),[139] investigated on the sensing of NO\textsubscript{2} and O\textsubscript{3} using \textit{Tetrakis(alkylthio)phthalocyaninato} lutetium complexes. They reported that phthalocyanines (PCS) are organic semiconductors that have been identified as promising components for gas sensors. They are chemically sensitive to reactive gases and shows potential for chemical selectivity with manipulation of metal center and the substituent of functional groups on the organic ring. The I.V characteristic are presented for the exposure to different concentrations of the gases.

Ravishankar S. Dudhe et al., (2009),[140] investigated organic field effect transistors based on poly(3-hexylthiophene) and Cu(II) tetraphenylporphyrin composite as sensors for detection of vapours of nitrobased explosive compounds. Polymer microcantilevers offer a sensitive cost effective platform for explosive gas detection. These sensors with optical and electrical transduction mechanisms are designed and fabricated using SU-8 polymer and they further functionalized with appropriate coating for explosive detection. In conclusion, P3HT and organic composite (CuTPP) based OFETs are demonstrated as the sensors for nitrobased explosive compounds.

Santhosh Paul et al., (2009),[141] developed a sensor, where Polypyrrole(PPy) is chemically functionalized with 5,10,15,20-tetraphenyl-21H,23H-porphyrin Iron(III)chloride, (FeTPPCI) with special interest on detection of noxious carbon monoxide(CO)gas in ppm level. Controlled functionalization of PPy has been achieved with incorporation of various concentrations of porphyrin. The resulted semiconducting material is neatly characterized by different techniques such as UV-vis spectroscopy, FTIR, GFAAS, XRD, and EDAX. The CO gas interacted very fast
with the FeTPPCI functionalized PPy at room temperature (RT). The response is not unidirectional, but reverse and the response and recovery times are 12 sec and 169 sec. They reported that the optimum level of doping (1mol% of FeTPPCI) is established for the highest sensitivity and the detection level is as low as 100ppm.

E. Chevallier et al., (2010),[142] investigated on a new sensitive coating for surface acoustic wave (SAW) transducers based on diamond nano-particles functionalized with a zinc porphyrin complexes for the detection of nitroaromatic vapors. They revealed that the role of diamond nano particles is to offer a stable sp³ carbon porous matrix onto which metalloporphyrin receptor is immobilized. The functionalized matrix is deposited on the transducer surface, featuring high surface area. They reported that sensor shown a high sensitivity of typically 120HZ / ppb with a detection limit at 1ppb level towards 2,4-dinitrotolune (DNT) vapors. The cross sensitivity of the sensor is low when exposed to ethanol or moisture.

M.Penza et al., (2010),[143] investigated on the effect of the surface functionalization of the carbon nano tubes (CNT) networked films with a metalloporphyrin layer for gas sensing. They reported that the modified films exhibits an increased sensitivity of the electrical resistance towards the concentrations of common volatile compounds such as alcohols, amines, aromatics and ketones at room temperature. Principle component analysis (PCA) presents that the functionalization provides enough selectivity change to turn a triplicate of the same CNT film into an effective sensor array capable of the compound recognition.

In the above works, porphyrins are used as functionalizing material in sensor devices for detecting volatile organic compounds, water vapour, pesticides, benzene, oxides of nitrogen, carbon monoxide, ethane, methane and explosives etc.
2.6 Motivation for the Present Research Work

It is observed from the literature survey that metal oxides, electrochemical, infrared, biosensors can be used for the detection of carbon monoxide. It is pertinent to point out that the above sensors have been used by the earlier researchers for detection of carbon monoxide in medical, process control and environmental applications. But no work has been reported so far, regarding the usage of bio-piezoresistive cantilever sensor for detection of carbon monoxide in the emission of automobile. Keeping in view of the importance of developing a carbon monoxide detecting sensor and in absence of earlier reported works in this area motivated the present investigation to develop a bio-piezoresistive cantilever sensor for detection of carbon monoxide in the emissions of automobiles. With this motivation the present research work was carried out with following specific objectives.

1. To fabricate a suitable piezoresistive cantilever.
2. To functionalize the cantilever sensor with suitable porphyrin which can detect carbon monoxide.
3. To develop an experimental set-up by incorporating the measuring and recording equipment to the cantilever biosensor.
4. To develop a suitable mounting for the sensor.
5. To carry out the experimental investigations with the above biosensor.
6. To analyse the experimental data and to draw conclusions from it.
7. To compare the biosensor developed by the present investigation with commercially available sensor used for detection of carbon monoxide in automobile vehicles.
8. To develop a handheld carbon monoxide detection instrument.

The experimental set-up and fabrication aspects are presented in Chapter-3.