Chapter 1

Review and scope of work

1 General introduction

The word ‘sensor’ is derived from the Latin word sentire, which means to perceive. It is a device that responds to external stimulus to convert it into an appropriate output signal mostly electrical in nature. The external stimulus may be physical or chemical. Depending on the external analyte and the nature of interaction, the sensor can be classified into two different categories: physical sensor and chemical sensor. Physical sensors respond to the physical parameters like heat, light, sound, pressure, magnetic field, current, etc. while the chemical sensors are used to monitor the environmental components like gas, vapors etc. Among the various materials utilized for sensors, semiconductor materials are very attractive ones because of their possible integration with signal processing unit for developing smart sensor. The important applications of these sensors are the monitoring of process parameters like automobiles,
telecommunications, computers and robotics, environmental monitoring and health care system.

In the past few years ‘integrated sensor’ that monolithically combine the sensor structure and some portion of the interface and signal-processing electronics on the same substrate have began to emerge. By the emergence of the smart sensors features such as standard interfaces, self-testing, fault tolerance and digital compensation using analog/softcomputing techniques it is now possible to improve the overall system accuracy, dynamic range and reliability while reducing capital and ownership costs. The concept is further extended to develop a sensor system on a chip that includes microactuators circuits, signal processing circuit for on chip compensation of different errors and display unit using opto-electronic material compatible to silicon IC technology. Another important aspect that has often been neglected in considering the advantages of sensor system on chip is that a variety of new sensors which were not practically applicable in the past, may now be used in many critical cases like biomedical, space and environmental applications.

Porous silicon (PS) is produced by chemical / electrochemical dissolution of crystalline silicon in a hydrofluoric acid based electrolyte by anodic etching. The resulting structure consists of three-phase mixture: silicon crystallites, silicon oxides and voids having dimensions ranging from nano to meso to micrometer. The dimensions of silicon rods and pores can be tuned for high sensitivity and rapid response time to particular vapor/gas molecules by simply controlling the formation parameters. Compare to metal oxide based sensors such as tin, zinc oxide, indium and alumina, the porous silicon offers higher
surface area to volume ratio and hence high reactivity to the vapors/gas molecules. Porosity can also be graded to provide zonal response to different stimuli, raising the possibility of multi sensor arrays, like full olfaction electronic nose. The possibility of the integration of sensor and signal processing unit onto silicon chips are proving powerful inducement to its further development.

1.1 Review of previous work on humidity sensing

Humidity measurement is one of the important tasks in many industrial processes for manufacturing of products such as textiles, food, paper, semiconductors, petrochemical industries and health care system. Recently it has been introduced into our daily life to make our living and working environments comfortable. For example, for ideal indoor-comfort, RH should be maintained between 35 to 65 % accordingly to published standards by the international standards organization (ISO). Water vapor also affects nearby proper operation of electronics circuit. Low humidity levels can result in electronics discharge (ESD), while high humidity levels may produce current leakage paths on printed circuit boards leading to premature device failures [1].

To fulfill the need of humidity sensing, the different humidity sensors exist for different applications [2-4]. The conventional humidity sensors are expensive and need extra electronics, the humidity sensor
using silicon standard CMOS fabrication is a low cost device and uses batch fabrication technology for its manufacturing process [5-7]. The important features are high sensitivity, low response and recovery time, low hysteresis, linearity, accuracy, high selectivity and low power consumption. Rittersma [8], F Genner and Zdankiewciz [1] and Chen Zhi et al. [9] have reviewed the different transduction techniques such as resistive, hygrometric, optical and most commonly capacitive utilized for developing miniaturized humidity sensors.

The relative humidity (RH) is defined as

$$RH = \frac{P_w}{P_s} \times 100$$

where $P_w$ is the vapor pressure and $P_s$ is the saturation pressure. Sometime it is represented as absolute humidity defined in gm/cm$^3$, which is the ratio of water in gm. with respect to the dry air.

The most important development in hygrometry was the invention of psychometer. It consist of two thermometers one in contact with liquid water, the so called ‘wet bulb’ and one placed in ambient air the ‘dry bulb’. The wet thermometer is kept moist by a cotton wick placed in a reservoir or as in modern psychometer, by a porous ceramic and a platinum resistance type thermometer. The accuracy of this type of hygrometer is better than 2 % RH and it remains inevitable for calibration procedures of other air humidity sensor [10-11].

Another well-known hygrometer is the Dunmore or LiCl dew point sensor [12]. This device is based on changes of the ionic conductivity that occur in a LiCl solution upon moisture uptake. The change in conductivity is measured by means of two fine thinned copper wires
wound around a thin walled glass tube, which is coated with dilute LiCl solution. One of the wires is connected to ac voltage source. To make LiCl salt conducting, the salt is heated by the heater element, which leads to evaporation and decrease of conductivity of the LiCl salt. This process continues until equilibrium between the moisture in the salt and air humidity is reached. The resistance is then measured by the second wire. From the saturation curve of LiCl, either the dew point or other humidity parameters can be calculated.

1.1.1 Hygrometric humidity sensors

Transduction from air humidity via the mechanical domain is one of the oldest techniques known. Hygrometric sensors exploit the volumetric changes of polymeric films [13]. Gerlach and Sager from Dresden University [14-15] report on a sensor design with a polymide thin film deposited on a micromachined silicon diaphragm that is similar to a piezoresistive pressure sensor. As the water content in the air increases the polymide swells due to the adsorption of water vapor. Due to difference in expansion coefficients of silicon/polysilicon and polymide, the bending of the membrane structured is changed. The latter is measured by the integrated piezoresistors. As compared to capacitive and conductive type devices, this sensor shows an improved long-term stability and less temperature dependence [16].
1.1.2 Gravimetric humidity sensors

The principle of resonance frequency in a vibrating mechanical structure can be used to sense the presence of vapors. The adsorption of water vapor results in a change of mass $\Delta m$, which changes the frequency of the beam. An important design aspect is the fact that the resonance frequency and Q factor of resonators are both functions of the total pressure [17]. If a mass is added to a structure vibrating at its natural resonance frequency, the resonance frequency will shift in proportional to the added mass. This is the working principle of gravimetric type sensor. It is of two types: the quartz crystal microbalance (QCM) and surface acoustic wave sensor (SAW). The QCM devices utilize longitudinal standing waves, known as thickness shear mode that propagates in the bulk of the material. In SAW sensors, resonance occurs as a standing wave within a thin surface of piezoelectric substrate. A few interesting devices have been presented with fullerene layers [18], sol-gel produced silica coatings [19], polymide [20] and porous ceramics. These devices are very much suited for measuring very low concentration of water vapor.

1.1.3 Optical humidity sensors

The physical background of optical humidity sensors is a harmonic electromagnetic wave. The moisture content in the air can be measured by measuring either the amplitude, or the polarization, or the frequency or the phase angle change of the incident wave in the medium [21]. Another use of the optical techniques makes use of the
absorption wavelength of water when light is passed through the vapor. The absorption of certain wavelengths provides information about the composition [21]. Water vapor can also be detected optically using a chilled mirror hygrometer, which is considered to be one of the fundamental measurement methods for water [22].

1.1.4 Resistive humidity sensors

Resistive humidity sensors are based on the change of conductivity upon vapor uptakes measured by current, voltage or the resistance. Mostly three types of materials like (i) ceramic (ii) polymer and (iii) electrolytes are used for resistive sensor. The properties of humidity sensors are reviewed in details by Traversa who distinguishes electronic and ionic interaction during their operation [23]. A great deal of works report on modeling and finding appropriate conducting materials [24-26] with interdigitated electrodes structure with some of them having integrated temperature compensation [27]. A polymer based conductive type hygrometer having interdigitated electrode covered with sensing materials was presented by Hijikigawa et at. [28] and H. Wang. et al. [29]. An electrolyte based humidity sensor using silicon substrate with platinum heater and Pt 500 temperature sensor in combination with a LiCl soaked polyvinyl alcohol and polymetha crylate (PMM) or PVA and polystyrene (PSt) was reported recently by Sakai et al. [30].
1.1.5 Capacitive humidity sensor

When vapor molecules are adsorbed, get diffused and condensed inside a porous material, the effective dielectric constant of the porous material changes. This change in effective dielectric constant changes the capacitance of the sensor. Today 75% of the total commercial humidity sensors are based on the capacitive technique [8]. The properties of the capacitive sensors depend on the hygroscopic material and the electrode geometries. Korvin et al. have proposed four electrode geometries like the interdigitated (IDE), mesh, spiral and grid for the humidity sensor [31]. The interdigitated electrode is favorable for rapid responses but a thin top electrode typically 10 – 80 nm Au will result in a more uniform field distribution. The equivalent circuit of a capacitive sensor consists of a capacitance parallel to the lossy resistance with series contact resistance [32, 33]. In a porous dielectric, as the air in the voids is replaced by condensed vapor with increasing the concentration of humidity, the sensor output increases nonlinearly. The absorbing properties of the porous dielectric can be approximated with models applying to dielectric mixtures [34, 35]. Because of very large surface to volume ratio and abundant void fraction very high sensitivity can be obtained with porous ceramic. Reviews of ceramic materials for developing humidity sensors have been presented by Seiyama et al. [36] and Traversa [23]. A tremendous amount of research has been dedicated to investigate different materials compositions and process parameters leading to optimal morphology [37-41]. The porous ceramic Al$_2$O$_3$ formed by electrochemical etching of aluminum under anodic bias exhibiting a pore size distribution that
depends on the formation parameters [42] has been utilized for developing commercial humidity sensors. The response time of such sensor is limited by diffusion mechanism and since the material is sensitive to dust and smoke, it requires maintenance by heating with refreshing resistors. A rather novel material for capacitive humidity sensing is the porous silicon (PS), which is formed by electrochemical or stain etching of silicon in hydrofluoric acid [43-46].

The detection of trace moisture concentration in gases is important both for atmospheric chemistry research and in industry, especially fast trace moisture detectors are required in the semiconductor industry, where water vapor is serious contaminants [47]. Various moisture sensors such as electrolyte and organic polymer [48], diode laser adsorption spectrometer [47], ceramic and alumina thin films [49-51] are commonly used to measure moisture content in gases at the ppm level.

1.2 Literature review of signal processing of a sensor

Most of the applications require that sensors should be sensitive, have short response time, good reproducibility and very small hysteresis. In addition, for an easy digital interface for direct digital read out, the response characteristics of the sensor should be linear and independent of temperature. There are two approaches for minimizing different non-idealities of sensor, one is the processing of the sensing material and the second is
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the signal conditioning and signal processing of the electrical output signal proportional to physical parameter to be measured. In the first approach, the morphology of the sensing layer should be optimized through formation parameters in such a way that nonlinearity, hysteresis, response time and offset are minimized. Widening the pore size in PS structure by changing the formation parameters, the response time, nonlinearity and hysteresis will be improved slightly but the sensitivity of the sensor is also affected [52]. Secondly, by integrating a thermo resistor might solve the hysteresis and temperature problems slightly, but the heating element around the sensing layer will change the long-term stability of the sensor due to change in capacitance and resistance of the sensor [8]. In the signal conditioning part, some of the errors like zero offset, interference to parasitic earth capacitance for capacitive sensor and sensor output change due to fluctuation of input reference signal can be reduced by using suitable electronics circuit [53]. Other errors such as nonlinearity, hysteresis and drift due to temperature can be compensated using suitable signal processing technique. The signal processing technique for compensation can be either analog compensation or digital compensation or based on different soft computing techniques [8, 54-56]. Analog compensations are based on changing the actual analog signal transfer function mostly through the trimmable resistors. The modification of analog transfer function is also possible by using digitally programmable array of resistors or capacitors. Diode function generator is one of the analog techniques is used to give piece wise linear output of a sensor. A multiplier /divider or multifunction module with summing opamp can be used to generate
polynomial function for the sensor response linearization. The disadvantages of the analog techniques are circuit complexity, limited resolution and lack of flexibility [55]. Moreover, they have limited capabilities to handle the nonlinearity and cross sensitivity problems. Because of their programmability, digital techniques using microcontroller or FPGA provide the accurate and versatile means for sensor response linearization and hysteresis error compensation. Moreover due to availability of microcontroller / FPGA chip, smart sensor with digital microcontroller / FPGA compatible outputs makes integrated calibration of the smart sensor possible [55]. The digital method can be either look up table or calibration function based technique. In ROM based digital technique, for the entire dynamic range of the sensor, the conversion table is stored in the ROM. The digital equivalent of the measurand is obtained by addressing the look up table by an m bit counter. In other digital method, a nonlinear coding scheme is used with the help of D/A converter and the measurand (humidity) is linearly encoded by a nonlinear decoding function. Both the techniques have the limitation in case of recalibration where, either full rewriting of the look up table and/or modification of the decoding function is needed. This is due to drift in sensor output for environmental effects, which introduce additional nonlinearity to the sensor output. In case of replacement and aging of sensor, the data stored in the memory is required to be updated and also these techniques are memory intensive [57-58]. Another widely used approach has been to use compensating algorithm. In this approach, the sensor output response is modeled using polynomial curve fitting technique. Here only the coefficients of the polynomial function are to
be stored and thus memory requirement is drastically reduced, but it involve matrix inversion operation which is computational and also it is unable to provide required accuracy even higher order polynomial is utilized [55,58]. In addition to this, the traditional statistical techniques are not adaptive but typically process training data simultaneously before being used with new data [56-59]. Very recently, soft computing approach like artificial neural network (ANN) technique has become popular to compensate different non-idealities such as nonlinearity, temperature error, hysteresis and drift of sensors [56-57,60]. In an attempt to find a compromise between the memories intensive look up table approach and the poor accuracy of the polynomial fitting method, the possibility of using ANN technique in compensating different errors of the sensor characteristics can be investigated [61]. Software technique by ANN gives better flexibility for sensor response linearization, hysteresis and temperature compensation and successfully applied for compensating them for different types of pressure, temperature and humidity sensors. For nonlinearity compensation, the sensor output is the input to the network and input to the sensor (measurand) is the desired output of the network. The network is trained by least mean square (LMS) algorithm in such a way that the transfer function of the combine sensor and ANN module is unity and thus the sensor nonlinearity is neutralized automatically. Artificial neural network is now well-established technique to obtain functional approximation between input and output of a [57, 61] sensor. The main characteristics of this approximation are that a function to be obtained is given through a set of input output pairs named training data set obtained from experiment. In this context ANN gives lower
interpolation error than conventional interpolation technique [56]. Due to self-learning ability and fault tolerance capability due to structural parallelism of the ANN and adaptability due to change in environment, it eliminates the use of complex and difficult mathematical analysis [62]. Damage to a few nodes or links thus need not impair overall performance significantly. Another interest of ANN model is that the model parameters can be updated on line to accommodate changing operating conditions due to environment [61].

1.3 Literature review for multiple vapors sensing using sensor array

1.3.1 Material aspects of the sensor array

The most important requirement for a sensor is that it should not only be sensitive to the particular vapor or gas molecules under measurement but also be selective with respect to other molecules. For practical field application, the sensor not only shows the sensitivity to the vapor or gas of interest but also have sufficient cross sensitivity for the other vapor present in the working environment of the sensor. This cross sensitivity is one of the concerns to the research community and some authors have addressed this issue and have proposed a multiparametric strategy [63-64] where more than one physical sensing parameters of the sensor can be utilized to enhance the selectivity of the sensor. However, the cross sensitivity of a sensor to different vapor molecules can be utilized effectively to develop sensor consisting of multiple sensing unit with different sensitivity and selectivity. The
sensor array approach [65-67] provides greatly increased selectivity and reliability in the field environment over a single sensor.

A sensor array called an electronic nose is an instrument that combines gas/vapor sensor arrays and pattern recognition analysis techniques for the selective detection, identification and quantification of individual components in a mixture of air pollutants or organic compounds or toxic gases in different environments [68-69]. Four approaches can be adopted for studying selectivity in developing sensor array namely

(i) Similar sensitivity layers investigated as coating on different transducers

(ii) The same sensitive layer investigated with a single transducer, recording of different physical properties

(iii) The same sensitive layer and transducer, same physical property investigated by different modes of operation [70-71].

(iv) Similar sensitivity layer but of different structure leading to different in output of sensor physical parameters.

Measuring different physical properties with optimized transducer like interdigitated structures to measure change in capacitance, quartz microbalances to measure change in mass, refractive interference spectroscopy to measure optical properties, calorimetric devices to measure change in temperature allows to characterize selectivity of non-conducting polymer which is used as identical coating on all transducer are reported by Haug et al.[72]. Weimar et al. [73] reports measurement of CO and humidity concentration using a single Figaro gas sensor by simultaneously work function, conductance and catalytic activity. A successful identification of CO and NO₂ in the ambient
atmosphere by means of pulsed temperature operated single tin oxide sensors was presented by Heily et al. [74]. Chemical vapors detection, classification and estimation using an array of conducting polymers or carbon black by utilizing single parameter sensing are well known [75-76]. Small numbers of carefully chosen detectors are thought to be sufficient because it is hypothesized that additional detectors add noise, instead of classification ability. In contrast, others have hypothesized that it is desirable to have larger number of detectors in the array to give proper representation of the features of the vapors in the mixture [77-78]. Current researchers suggest that in mammalian olfaction, there are approximately $10^3$ different receptors genes and approximately $10^7$ total reception cells [79]. Thus it is not clear whether small sensors with high selectivity or purge sensors low selectivity will be appropriate for the sensor array.

Different types of materials are employed for developing the sensor array in different applications.

In conductive type sensor array, the sensing units are made of carbon black or non-conducting polymers [75-76]. Exposure to particular analyte causes the sensing unit to swell by different amounts resulting the change in electrical resistance. By employing different polymers, a large number of different, broadly tuned sensors can be fabricated and does not require external excitation or complicated signal processing like optical sensing [80]. On the other hand, in capacitive gas sensor array, due to adsorption of gas molecules, the effective dielectric properties of the polymer material change [81]. Yamazoe et al. [82] utilized solid electrolyte potentiometric sensors for the real time detection of air pollutants. M. Pardo et al. [83,] and A.
Branca et al. [84] have developed an electronic nose using metal oxide material like SnO2 for the classification of different brands of espresso coffee and discrimination of perfumery compound in fragrance respectively. Very recently Stainlaw Osowski et al. [85] reports the monitoring of the different air pollutants of CO, CH₄, ethanol, hydrogen, LPG, Butane using metal oxide based sensor array.

PS based optical sensor array with ellipsometric readout for monitoring the gas concentration has been proposed by Wang and Arwin [86]. In such an array the different sensing layer are formed by deposition of copper and its oxide on PS to detect vapor like methanol, ethanol, and 2-propanol. By analyzing the changes in the ellipsometric angles, gas pattern recognition and measurements of concentrations can be achieved. For this purpose PS layers with different sensitivities and selectivity to the target gases are prepared by deposition of copper and copper oxide inside the porous layer. Very recently Lewis et al. [87] have proposed the development of a conductometric PS gas sensor array with different selective and sensitive layers formed by electroless deposition of tin and gold for sensing gases like NOₓ, NH₃ and NO.

1.3.2 Signal processing of the sensor array

Although in a sensor array each individual sensor is tuned to a specific chemical vapor/gas, each sensor responds to a wide variety of chemical vapors in the mixture. Collectively, these sensors respond with a unique pattern to all analytes. The analysis of the unique pattern can be split into four sequential stages: (i) signal preprocessing, (ii)
dimensionality reduction, (iii) prediction and (iv) validation. Initial part in the array is the hardware element, which typically consists of a sensor array, a pattern delivering subsystem, an electronic instrumentation stage and a computer for a data acquisition. The process of data analysis starts after the array finger prints have been acquired and stored into the computer. The first computational stage is called signal preprocessing, which includes compensation of sensor drift [88-89] extracting describing parameters from the sensor array response and preparing the feature vector for further processing [69,90-91]. A dimensionality reduction stage projects this initial feature vector onto a lower dimension space in order to avoid problems associated with high dimensional parse data set. The resulting lower dimensional but more informative data is then used to a given prediction problem typically classification, regression or clustering [69]. The classification tasks address the problem of identifying an unknown vapor/gas as one from a set of previously learned odorants. In regression task, the goal is to predict a set of properties like concentration, quality for an analyte, typically complex moisture of vapors. Finally, in clustering task, the goal is to learn the structural relationships among different vapors. A final step is the selection of models and parameters setting and the estimation of the true error rates for a trained model by means of validation techniques.

Neural network or neuro-fuzzy hybrid neural network coupled with nonsupervised principal component analysis (PCA) are most widely used techniques in gas/vapor analysis systems [85, 92-93]. Very recently some authors have applied other softcomputing techniques like wavelet [94], genetic algorithm [95], independent component
analysis [96] and support vector machine (SVM) and neural network for identifying the vapor in mixture [97]. Very recently E. Llobet et al. [93, 98] has cascaded fuzzy ARTMAP classifier with genetic algorithm to analyze the binary mixture of three volatile organic compounds using metal oxide gas sensor array.

The goal of a pattern classifier is to generate a class label prediction for an unknown feature from a discrete set of previously learned classes. It can be shown that to minimize classification errors one should assign example to a particular class with the largest posterior probability [90]. This is known as the maximum a posterior (MAP) rule and is the best any classifier can do.

The K-nearest neighbors (KNN) rule is also a powerful technique that can be used to generate highly nonlinear classifier with limited data. To classify the unknown pattern KNN finds the closest examples in the data and selects the predominant class among these K neighbors. The main limitations of KNN are (i) storage requirements since the entire data needs to be available during recall (ii) Computational cost, since for each unlabeled example/class the distance to all training examples needs to be computed (and stored).

Multi layer perceptron (MLPs), the most popular type artificial neural network are feed-forward networks of simple processing elements or neurons whose connectivity resembles that of biological neural circuitry. Each neuron in an MLP performs a weighted sum of its inputs and transforms it through a nonlinear activation function, typically sigmoidal. An MLP is able to learn arbitrarily complex nonlinear regressions by adjusting its weights in the network by a gradient descent technique known as back propagation of errors. At
each stage in the training process, the MLP process all of its input in a feed-forward fashion, compares the resulting outputs with the desired ones and back propagates these errors to adjust each weight in the network according to its contribution to the overall error. A number of heuristics are available to improve the operation of back propagation [90]. To avoid over fitting, the complexity of the MLP can be controlled by limiting the network size. With the number of inputs and outputs determined by the application, the network size is strictly a function of the number of hidden layer and hidden neurons per layer. A single hidden layer MLP can approximate any classification boundaries with arbitrary accuracy provided that the number of hidden units is large enough but the addition extra of hidden layers may allow the MLP to perform an efficient approximation with fewer weights [99-100, 94-95]. In practice, the constructive approaches which start with a small MLP and incrementally add hidden neurons or pruning approach, which start with a relatively large MLP and sequentially remove weights, can also be employed [101,96]. However, the optimum MLP structure depends on multiple factors including complexity of the classification problem, number of inputs and outputs, activation function, training algorithm and level of noise in the data. Training with noise also known as jitter, can be used to prevent the MLP from approximating the training set too closely and has been shown to improve generalization [69].

Radial basis functions (RBF) are also feed-forward connectionist architectures consisting of a hidden layer of radial kernels and output layer with linear activation function neuron [100]. Each hidden neurons in an RBF is tuned to respond to a local region of feature space by means of a radially symmetric function such as the
Gaussian. The output units, on the other hand, form linear combinations of the hidden units to predict the output variable in a similar fashion to MLPs. RBFs are typically trained using a hybrid algorithm that employs unsupervised learning for the hidden layer followed by supervised learning of the output layer. MLP and RBF are the two most popular types of neural network architecture employed in the e-nose community and both models can function as universal approximator.

A few more approaches hold a promising feature for the processing of sensor array data, particularly fuzzy logic, independent component analysis (ICA), support vector machine (SVM), adaptive and biological cybernetics paradigm [93-94]. Fuzzy logic provides a framework for representing uncertainty in a sensor data, model parameters and outputs. The use of fuzzy logic and neurofuzzy logic has been applied for analyzing sensor array data [93]. Independent component analysis (ICA) is a multivariate statistical tool, which in the last few years has drawn considerable attention in the research field such as neural network, signal processing and blind source separation [96].

Adaptive techniques, particularly adaptive resonance theory (ART) provides mechanism that solves the stability-plasticity dilemma which refers to the inability of most learning systems to adapt to changing environments without comprising previously acquired knowledge [102-103].
1.4 The material porous silicon (PS)

Porous silicon (PS) is a natural nanostructured material that can be prepared easily by using crystalline silicon substrate. PS was discovered by Ulhir at Bell Lab, USA in 1956 [104]. Recently the researchers particularly in silicon microsystem technology show increasing interest for its multifaceted applications in different areas like sensing devices [105], opto-electronics [106], ultrasonic devices [107], microbiology [108-109], microengineering [106], astrophysics [110], signal processing [111] and medicine [112]. Due to these multi-functional applications of PS, recently it has been proposed to be an educational vehicle for introducing nanotechnology and interdisciplinary material science by eminent scientists working in this field [113].

1.4.1 Formation of porous silicon and its structural morphology

Several methods are developed to make the porous layer with wide variation of pore morphologies having pore dimensions from nano to meso to micro. Pure chemical etching of silicon using mixture solution of HF, HNO\textsubscript{3} and water [106,114], NaNO\textsubscript{2} and HF or CrO\textsubscript{3} and HF [115, 110] is employed for PS formation. However, the most widely used method is the electrochemical etching of silicon crystal in electrolyte solution of HF and ethanol or methanol [116] or HF and water or HF and N,N dimethyl formamide (DMF) [117] by passing current for a fixed duration of time. Hummel et al. [118] utilized a new
spark erosion technique for PS formation, which does not involve any aqueous solution or fluorine contaminants in air or in the other gases. Another interested development in this area is the magnetic field assisted anodization technique employed by Koshida et al. [119]. Very recently Y. Y. Xu, et al. [120] describes hydrothermal etching of crystalline silicon in HF containing ferric nitrate to obtain large quantities of regular, uniformly distributed silicon nano pillars which are perpendicular to the surface and well separated from each other. The pore morphology of the PS layer characterized by the void fraction or porosity, the mean size of the pores, the pore size distribution, the interconnectivity of the pores, the passivation and mean size of the skeleton enclosing the pores depends on formation parameters of the PS, additives in the electrolyte solution and doping concentration of the silicon wafer [121]. However, vertically grown uniform pores can also be developed in n type c-Si using photolithography [122].

1.4.2 Porous silicon as sensing devices

Discovery of photo and electroluminescence [112] in room temperature of PS arising due to the quantum confinement effect in the presence of an enlarged band gap creates interest among the researcher to exploit the material for different photonic, electro-optical and sensor applications. Once the different ways are being found to stabilize it sufficiently, many new and novel applications are constantly being reported.

Of the many sensors now in the advance stage of development, PS humidity sensors are based on the change in either conductivity or
dielectric constant that occurs when moisture is absorbed. These PS devices are proving more sensitive than conventional ceramic sensors that are used in this application and offer other favorable characteristics including, low hysteresis, short response time, and low power requirement [112]. A simple cheap gas detectors that are super-sensitive, could be based on resistive PS elements [123-124]. Researchers at the University of Brescia, have patented a technique using a PS membrane on alumina substrate which sense concentrations of NO$_2$ of 100 parts per billion (ppb) with minimum interference from contaminant organic vapors [112, 125], at low power and room temperature. Such sensitivities can be attributed to the PS ability to adsorb numerous molecules of the target gas or vapors into its large specific surface area. Often sensitivities can also be enhanced by surface derivitization like electrodeposition of copper sulphide coat film into microporous silicon to develop sensor that is responsive to ammonia with much high sensitivity than the semiconductor oxide and cuprous sulphide based films that are used conventionally. Introducing dyes into the cavities is another technique that can enhance sensitivity to specific molecules [117]. Very recently a conductometric porous silicon gas sensors consisting of a sensitive and selective surface layer formed by electroless metal deposition to form gold or tin oxide nanostructured framework interacting with the nanopore coated microporous surface utilized for rapid and reversible transduction of sub-ppm levels of gas analytes which includes CO (<5ppm), NO$_x$ (1<ppm), SO$_2$ (1<ppm) and NH$_3$ (500ppb) [103].

Another attraction of PS is that the fabrication techniques can be easily adapted from those used by the microelectronics industry. High
reactivity means that the material can easily be micromachined by etching and oxidation and readily be patterned by lithography processes.

It is also possible to coat the internal surfaces of PS with biomaterials that are attractive target molecules for developing biodetectors [126]. Oxidized PS layer has been reported as a novel and promising substrate material for biosensors [127]. PS’s biological properties make it possible to develop novel drug delivery systems as well that could offer more than a progressively degrading capsule. Derivitized PS mirrors placed under skin could be used in minimally invasive optical monitoring of biochemical markers for cancer disease treatment [112]. More recently, light addressable potentiometric sensors using PS, which is able to detect penicillin in low concentration has been realized [112]. Fauchet along with physician Alice Pentland in collaboration with the MIT, USA has developed ‘smart socks’ in which PS pressure sensor monitor blood pressure in the feet of diabetic patients [112]. It is also possible by using PS low cost disposable health care products in the form of tiny chips manufactured in thousands by established microelectronics technology. Crucial to selectivity, another PS attribute is the ability to tailor the material morphology to the desired application. Fine control can be achieved by specifying particular etching parameters so that micropores with different pore sizes suited to different molecules, can be tailored to the sensing capability required. Moreover, it has been proven practical to produce pores of graded size on the same substrate to achieve multiple target sensing capability on the same chip. Graded morphology is the key to multiple gas/vapor sensing capability within
the same array and the possibility of an ‘e-nose’. A compact, sensitive PS-based electronic nose could bring greater reliability and repeatability into the professional sensing of food and wine [112].

1.4.3 Porous silicon as a humidity / trace moisture sensor

The first investigations of humidity sensing of the PS layer were done by Anderson and his coworkers [45-46] and a parallel-plate capacitive sensor with PS as sensing layer was proposed by Richter [129]. A number of other authors have investigated the humidity sensing features of PS having integrated sensor, heater and temperature sensor fabricated using p-n junction diode [130-133]. Both conductive as well as capacitive type humidity sensor are possible. Recently, Foucaran et al. [134] proposed a PS capacitor in combination with a thermo electric cooler. Such structure enhances the condensation in the micropores and the dew point can be measured. Recent trend is to utilize the oxidized PS layer. It is known that hydrogen covered silicon surface is hydrophobic while the surface covered with imperfect oxide is hydrophilic [117, 135-137]. It is therefore expected that the oxidation strongly promotes capillary condensation of water vapors in the pores, which leads to overall increase in sensitivity [112, 137]. The details understanding of low condensation of water affects conductance and capacitance are reported in [137]. Y. Y. Xu et al. [120] have discussed the potentiality of a nanoporous pillar array formed by hydrothermally etched silicon in a
mixed solution of HF and Fe(NO3) for humidity sensing. It has been established that the humidity sensitivity of PS depends highly upon the morphology of the PS layer including the layer thickness, the size distribution and regularity of the surface morphology [120, 137-138]. In another novel work reported in [117] authors use mild oxidizer such as N,N, dimethyl formamide (DMF) for PS formation to obtain straight and smooth pore walls in the micrometer ranges for water vapor. Recently a PS based capacitive humidity sensor with a phase detection signal processing circuitry has been reported by J. Das et al. [139]. Comparison of porous silicon, porous polysilicon and porous silicon carbide as transducing element for humidity reported by Connoly et al. [140] show that the sensitivities close to 200-300% for a single crystal device can be achieved but the effect of ambient temperature is less for the porous polysilicon than for the single crystal silicon PS sensor. Both the materials have the advantage sensing parameters can be optimized independently of the electronics. Silicon carbide has the added advantage that it can withstand a range of harsh working environment.

Very recently T. Islam et al. [51] have studied the potentiality of the PS material for developing ppm level moisture sensor in the range of few ppm to several hundreds ppm. The performance of the PS ppm trace moisture sensor in dry gas are compared with the commercial porous alumina and it was proposed that by selecting optimum morphology by electrochemical formation parameters, PS can provide alternate CMOS integrable trace moisture sensor for commercial application. In a recent work reported in [141] J. Salonen and his coworkers have utilized thermal carbonized PS sensor for measuring
sub ppm moisture in the range of 1000 to 6000 ppm. The thermal carbonization of the PS layer replace the chemically reactive Si-H bonds with more stable Si-C bond thus help to stabilize the PS layer for sensing applications [141].

1.5 Scope of the work for the present study

From the above discussions it is very much clear that PS is an excellent transducing material for vapor sensing application. By tuning the pore morphology of PS, different vapors can be detected selectively. This feature can be utilized for developing PS vapor sensor array for e-nose application. In the present study, suitable instrumentation system for precise measurement of capacitive impedance of PS layer in vapor is developed. The detection circuit is based on phase detection principle, which can give output in proportional to phase angle change due to change in capacitive impedance of PS layer in presence of vapor molecules. The circuit can also minimize the interference to parasitic earth capacitance and offset error.

The PS capacitive sensor with suitable pore morphology has been designed, fabricated and tested to detect the moisture content in the dry gas in the range of 0 – 200 ppm and the results are compare with the commercial ppm level trace moisture sensor like thin film alumina sensor. Though PS is very useful material for different sensing application but the linearity, hysteresis, and response time are still subject to further improvements [8]. In addition, the slow oxidation of
the PS layer changes continuously the morphology of the layer leading to the drift in sensor output with the passage of time [136].

The different nonidealities of the PS humidity sensor like nonlinearity, hysteresis, drift due to aging and temperature dependence are studied in details and suitable signal processing systems using ANN based soft computing technique are proposed for compensating them. The compensating ANN models for the error compensations of the sensor are then hardware implemented using microcontroller or FPGA. Efforts are also made to ASIC implement the MLP ANN network with tansigmoidal activation function utilized for developing an integrated signal processing system for compensating nonlinearity, temperature and time dependent drift due to aging for smart PS humidity sensor.

Finally, a PS based sensor array for sensing organic vapors like methanol, ethanol, isopropanol and water vapor have been designed, fabricated and tested. The experimental results of the array are then analyzed by two techniques (i) matrix diagonalization (ii) a multiparametric ANN based pattern recognition technique with non supervised principal component data analysis (PCA), where multiparametric approach improves the accuracy of identification by including more features of the array in the data matrix and PCA analysis helps to reduce the complexity of data matrix by extracting more informative data from array data base. Possible hardware implementation of the signal processing systems required for identification and estimation is also discussed.
1.5.1 Porous silicon

A number of studies made by SEM [142], XRD [143], TEM [115] and AFM [144] exist in the literature for the structural pore morphology of PS formed on either p or n type silicon wafer. Very recently, some authors paid attention on the uniformity, pore branching and vertical growth of the pores in the PS layer for sensor application [115]. Furthermore, a study on the improvement of long-term stability of PS layer by low temperature ambient condition or different oxidizing agent has been performed using PL and IR measurements [145].

It is well known that capacitance and conductance variation of porous silicon significantly depend on the size and distribution of pores [137]. Thus morphology of the PS layer plays an important role in determining the sensitivity, response time, recovery time and nonlinearity and hysteresis [138]. The porosity and morphology of the PS can be varied by controlling the formation parameters, doping concentration, and intensity and wavelength of illumination [112,137]. The morphology of PS layer is tuned for utilizing the PS for sensing trace moisture in dry gas. Efforts are made to select optimal formation parameter to optimize the performance of the PS sensor with respect to commercial (SHAW) thin film porous alumina moisture sensor. A precise instrumentation for the quantitative estimation of the exact concentration of the moisture is also developed.

In chapter 2, design, fabrication and characterization of the PS based moisture sensor has been reported. Studies have also been made to select the optimal pore morphology so that the sensor characteristics
can be optimized by selecting different pore morphologies utilized for moisture sensing in ppm volume (ppmV).

1.5.2 **Role of parasitics and precise instrumentation systems**

PS is a nanostructure semiconductor having both capacitance and conductance, which depend significantly on the presence on intercapacitances and resistances arising [139] out of the contacts between different layers and interconnects of the sensor. The desired capacitance is also affected due to the presence of unavoidable parasitic earth capacitance with respect to ground. Initial offset capacitance and resistance of the sensor at dry condition also affects the output of the sensor.

**Chapter 3** aims at developing a precise instrumentation with parasitic earth capacitance and offset error compensated output. With the optimized signal frequency [139], two simple but precise circuits: (i) based on the signal amplitude measurement and (ii) the other based on phase detection principle have been developed. The first one called active bridge technique measures the signal amplitude varying according to the variation of PS capacitive impedance in presence of water vapor. The second circuit measures the phase shift of a sinusoidal signal passing through the PS sensor [105]. The phase detection circuit has the advantage that the output is independent of fluctuation of the amplitude of reference signal and can detect the change in phase angle resulting from the change in capacitive
impedance of the PS dielectric in presence of vapors. The circuit utilizes electronics components, which can be ASIC implemented.

1.5.3 Compensation of nonlinearity and hysteresis errors of a PS humidity sensor using ANN technique

The quality of a PS sensor can be analyzed by its characteristics: like response time, recovery time, sensitivity, nonlinearity, hysteresis, and temperature range and time dependent long-term drift due to aging [8]. Thus PS based sensor for its commercial usefulness must fulfill number of requirements: they have to respond and recover quickly, sensitivity should be large, their temperature dependence should be negligible, nonlinearity and hysteresis errors should be as low as possible and the time dependent drift due to aging should be very small. But a practical PS sensor exhibits nonidealities such as nonlinearity, hysteresis and drift due to aging [8]. The errors can be compensated by adopting two approaches (1) by processing the material i.e. controlling the pore morphology through chemical etching for example widening the pore size of the PS, hysteresis, nonlinearity and response time can be improved but the larger pores affect the sensitivity of the sensor also [138], (2) by processing the sensor output signal by utilizing signal processing techniques.

Chapter 4 aims at developing artificial neural network (ANN) based software technique to compensate the nonlinearity and hysteresis errors. For the compensation of errors, a PS humidity sensor with suitable formation parameters have been designed, fabricated and
characterized. Normally for the characterization of the sensor, the metal contacts are made on the PS surface itself. But proper ohmic contacts having reproducible i-v curve is still an existing challenge for PS devices and is very much essential for all types of sensors [117, 138]. A capacitive porous silicon (PS) vapor sensor has been developed on a single crystal p-type silicon substrate in which novel metal contacts are made exclusively on the silicon substrate.

1.5.4 Study of long-term drift of a PS humidity sensor and its compensation using ANN technique

Aging of porous silicon material is another important constraint for its large-scale commercial use [136,146]. It is related to aging of the sensor material, which is irreversible change in the electrical, mechanical, and thermal properties of the material over a long period of time. The aging of PS is due to incomplete oxidation of PS layer [145]. The effect of aging is to change in pore morphology with the passage of time, which results drift in sensor output. The drift due to aging can also be minimized by adopting either stabilizing the PS layer or post oxidization of PS layer in different oxidizing methods. The oxidation of PS layer may be in H$_2$O$_2$ [117] solution, or keeping the sample in room temperature for some time or thermal oxidation in inert gas [136] or thermal carbonization [138]. However, these techniques can not stabilize the PS layer completely [136], hence the post oxidized sensor with signal processing will be the most suitable way of aging compensation.
Chapter 5 aims at studying the drift in sensor output with the passage of time. Three PS samples with identical formation parameters: one freshly prepared and washed in deionized water, second freshly prepared and oxidized in H$_2$O$_2$ for 48 hours in room temperature and third oxidized in room temperature air for 1 yr. are utilized.

A compensating model based on adaptive linear neural network (ADALINE) was developed for compensating the drift due to aging of the PS sensor. The compensation is based on periodic recalibration for the estimation of the drift with the help of standard humidity sensor. Finally a scheme using multi layer perceptron (MLP) for integrated nonlinearity, temperature and drift compensation is proposed.

1.5.5 Hardware implementation of the compensating algorithms

To obtain the nonlinearity and hysteresis compensated output of the PS humidity sensor, the ANN models developed for the error compensation discussed in the chapter 4 are implemented using microcontroller.

For drift compensation, the entire dynamic range of the humidity sensor is divided into two parts, ADALINE neural network is utilized to obtain polynomial function for each part. The polynomial functions are then hardware implemented using electronics components.

Finally a scheme developed using multi layer perceptron neural network to obtain an integrated drift and temperature compensated linear output. Then the scheme is hardware implemented using FPGA
chip and ultimately, the MLP network utilized for this purpose is ASIC implemented for developing smart humidity sensor.

Thus chapter 6 discusses the details hardware implementation of the different ANN models for errors compensation of a PS humidity sensor using analog IC / microncontroller / FPGA chip. The ASIC implementation of the MLP model for integrated signal processing system is also discussed.

1.5.6 Development of vapor sensor array with its signal processing systems

The sensitivity of a PS capacitive sensor for different vapors depends significantly on the pore dimensions and pore morphology of the porous structure as well as various physical parameters of the vapors like molecular dimension, molecular weights, surface tension, dielectric constant, dipole moment, electronic polarizability, polar or non-polar molecules [51,117]. The structure dependent sensitivity and selectivity of the PS sensor leads to the possibility of developing PS based vapor sensor array.

In chapter 7, we have studied on the selectivity and sensitivity of an array of four PS sensing layers having different pore morphology and porosity for sensing of methanol, ethanol, isopropanol and water vapors.

The output of the array is a unique fingerprint analyzed by two techniques: (1) matrix diagonalization (2) multiparameter approach by multi-layer perceptron (MLP) based pattern recognition with non
supervised principal component analysis (PCA). The signal-processing technique of the array is hardware implemented using analog IC/microcontroller for an embedded system.

Finally, the last chapter summaries the important observations and concludes the work done in previous chapters. Also the scope of future work is indicated.

References


Chapter 1: Review and scope of work

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