Porous Silicon Sensors- Elusive and Erudite

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Abstract: Porous Silicon Sensors have been fabricated and tested successfully over the last few years as humidity sensors, vapour sensors, gas sensors, piezoresistive pressure sensors and bio- sensors. In each case it has displayed remarkably sensitivity, relatively low temperature operation and ease of fabrication. Brief description of fabrication and properties of all these types of different sensors is reported in this paper. The barriers of porous silicon like contact, non- uniformity, instability etc. are also discussed.

Keywords: Porous Silicon , Sensing application, Barriers of porous silicon

1.Introduction

Porous silicon is one of the most attractive host platforms for fabrication of large variety of sensors [1]. Its widely different structures (from macroporous of mesoporous to nanoporous) having very large surface to volume ratio, ease of fabrication, distributed nature of resistive capacitance network, natural nanocrystalline quantum wire like behavior and compatibility to silicon IC technology leading to smart sensors have been fascinating the sensor researchers of all over the world for more than a decade [2-6]. Extensive work has been reported on humidity sensors, organic vapour sensors and gas sensors with porous silicon as host material [5-12]. Porous silicon has also been used as a sacrificial material for the fabrication of inertial sensors like pressure sensors [13]. Recently it is reported that nanocrystalline porous silicon exhibits a very high piezoresistivity that can be utilized for the fabrication of high sensitivity pressure sensors[14-15]. Macroporous silicon based biosensors have been drawing serious attention of the researchers over the last few years [16-20]. Instantaneous detection and quantification of bacteria and other organic materials including DNA measured through the change of the electrical impedance of porous silicon sensor have been reported by several groups [21].

Inspite of the demonstrated high potential of porous silicon as an excellent host platform for sensing applications, commercial availability of porous silicon sensors are yet to be realized.

The secondary limitations of porous silicon like nonlinearity, temperature sensitivity, drift, hysteresis etc. can be overcome through ingenious and intelligent electronics that may be hybridized or integrated with the porous silicon sensor as desired [22-23]. But the primary limitations of porous silicon originate from the problems of (a) stable ohmic contact (b) instability of porous silicon material characteristics (c) lack of reproducibility. In this presentation fabrication of porous silicon and its applications as different types of sensors are first reported. Various problems associated with porous silicon are then discussed and the directions of work towards their solutions are pointed out.

2.Formation of Porous Silicon

Porous Silicon can be formed either nanoporous or mesoporous or macroporous structures depending on the formation parameters and the forming solution. The experimental details for forming both nanoporous and macroporous porous silicon are reported here.

2.1Nanoporous Silicon

On a p-type monocrystalline silicon wafer of resistivity 1-2Ωcm, porous silicon is formed by anodic etching method [1]. The anodic bath is composed of a mixture of HF (48%) and ethanol. The formation current density and time of formation used for anodic etching are 10-50mA/cm^2 and 10-30 minutes respectively. A porosity (*P*) of around 40- 80% and a thickness (*t*) of 10-50μm have been obtained with the above formation parameters. The microstructure of the porous silicon shown in Fig2. 1 displays nanostructure of silicon in the range of 20-70 nm.

2.2Macroporous layer formation

For macro porous layer formation the porous silicon layers are fabricated by electrochemical etching of p-type silicon (ρ 10-20Ωcm) under constant current conditions with a current density of 4mA/cm^{2}using the electrolyte of 4wt% hydrofluoric acid in N,N dimethylformamide (DMF). The use of a mild oxidizer such as DMF results in straight and smooth pore walls with pore diameter in the micrometer range. The porous layers are etched for 60 minutes resulting in 15-20μm thick layers. The macroporous structure of the porous silicon layer is shown in Fig.2.2 A thin layer of surface oxide is sometimes required for stable operation of the devices For the growth of conformal oxide layer anodic oxidation of porous silicon may be done. [16]. After oxidation, the porous layers are rinsed with deionized water and ethanol and dried under a stream of nitrogen. The metal contacts in lateral fashion on

porous silicon are then deposited by vacuum evaporation followed by gold contacts for wire bonding.

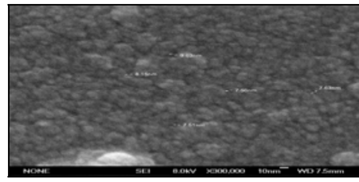


Fig.2.1 Nanoporous Structure

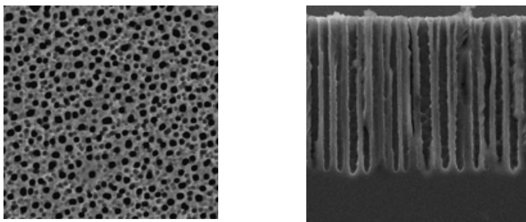


Fig.2.2 Macroporous structure

3.Vapour Sensors

One of the earliest applications of porous silicon sensors is vapour sensors including humidity sensors. PS based vapour sensors must fulfill a number of requirements: they have to respond quickly, sensitively and accurately, their temperature ranges should be as large as possible and they should have desired selectivity with respect to other vapours or gases. It is well known that both capacitance and conductance variation of a porous ceramic layer depends very much on the porosity of the layer. The size and distribution of pores of the ceramic sensors also play very important role in determining the sensitivity and response time [1]. The porosity and pore morphology of PS can be varied from mesopores to micropores and to nanopores by simply controlling its formation parameters like concentration of electrolyte, etching current density, etching time, bulk doping of the silicon wafer and intensity and wavelength of illumination [2]. Thus, in PS based vapour sensors, different vapours can be sensed selectively and sensitively by tailoring the morphology and the corresponding adsorbing properties of PS sensing layer.

3.1Principle of vapour sensing

The working principle of a PS based capacitive vapour sensor is straightforward: vapour molecules are first adsorbed at the surface of PS transducing layer and then diffuse into the porous bulk. Condensation of the diffused vapour may occur inside the pores having radii less than a critical value called Kelvin radius [5]. Due to the differences in permittivity, the capacitance of the layer changes as a function of the vapour uptake, which is directly related to the vapour concentration level in the environment [6].

In order to explain the change in dielectric constant of PS layer and provide a theoretical basis for optimizing the porosity and pore morphology of the PS transducer for sensing a particular vapour selectively, a theoretical model has been proposed [3]. This model considers PS as a three-phase (silicon nano-particles, silicon oxides and voids) mixture of dispersed spherical particles. The sensitivity of PS layer to a particular vapour is due to the adsorption of the vapour molecules on its surface as well as condensation inside the pores. Thus, the adsorption-diffusion-condensation kinetics of the vapour molecules inside the porous bulk and consequently the change in dielectric constant of the porous layer has been modeled with a generalized effective medium approximation (GEMA)

3.2Fabrication of humidity sensor

Fig. 3.1 (a), (b) show respectively the schematic and actual photograph of PS humidity sensor. PS layer of 1cm X 1cm area has been fabricated on a p-type (100) (1-2 .cm resistivity) oxidized and polished silicon wafer by standard electrochemical etching method [1]. The formation current density and HF concentration in electrolyte were 10 mA/cm2 and 24% respectively and the sample was anodized for 3 minutes to achieve a porosity of the order of 75% [6]. Top metal contacts and micro heater were developed by vacuum evaporation of aluminium through a patterned shadow mask developed by standard photolithography [5]. Width of each IDE and the spacing between them were 1mm and 0.5mm respectively (Fig.3.1a, b, c). The output voltage of humidity sensors for different humidity is shown in Fig. 3.2.

3.3Principle of multiple vapour sensing

The sensitivity of PS capacitive sensors for different vapours depends significantly on the pore dimensions and pore morphology of the porous structure as well as various physical parameters of the vapours like molecular dimension, molecular weight, surface tension in the liquid phase etc. [3]. This structure dependent sensitivity of PS sensor leads to the concept of

PS-based vapour sensing array. In such an array, no individual detector responds solely to a specific molecule, but the collective response of the entire array of detectors yields a unique fingerprint for the vapour of interest [29]. Such arrays are often referred to as 'electronic nose' and are not designated in advance to perform a specific task, but are instead developed to identify and quantify vapours based on various signal-processing techniques [30]. This approach to vapour sensing takes advantage of the collective output of an array of broadly responsive detectors. We have studied on the selectivity and sensitivity of an array of four PS sensors having different porosity for sensing of methanol, ethanol, iso-propyl alcohol and water vapours. Matrix diagonalization method has been used for analysis of the vapours.[29].

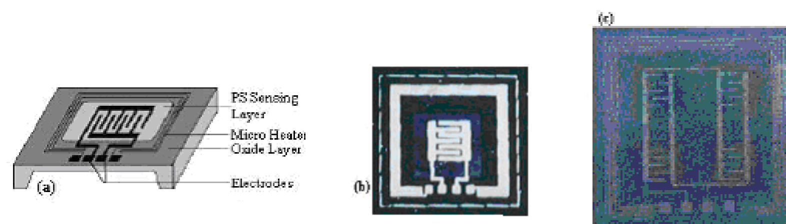


Fig. 3.1: a) Schematic and actual photograph of PS Humidity Sensor with (b) single PS layer and (c) four PS layers.

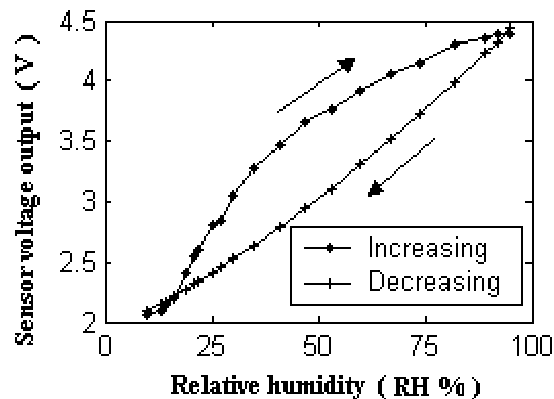


Fig 3.2: Response of porous silicon humidity sensor with the variation of humidity.

3.3.1 Fabrication of Sensor Array

An array of four PS layers has been fabricated on an (100) oriented oxidized polished silicon wafer having resistivity 1-2 Ωcm. The PS layers were formed by standard electrochemical etching in HF based electrolyte through proper masking.. The porosity of different layers has been varied in the range of 40%-75% by controlling the formation parameters and post formation treatments [30].. Fig. 3.3 shows the top view of the actual PS transducer array.

Around the active PS/IDE area, a metal heater has been deposited. This heater acts as the refresh resistor that accelerates the out diffusion and desorption process of the vapours condensed inside the porous network.

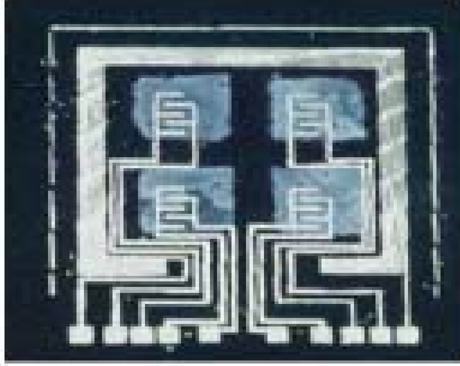


Fig. 3.3: Photograph (top view) of the PS transducer array.

3.4Vapour Identification

For vapour identification using this PS based sensor array the array has been placed inside the chamber that can be evacuated with a rotary pump and is connected with a flask containing the liquid that has to be sensed in vapour phase. The flask is placed on a heater. External contacts with each of the sensing layer and the refresh resistor have been established with pneumatic probes (pressure contacts). The chamber has been evacuated to 0.1 torr pressure in each case and then exposed to methanol, ethanol, iso-propyl alcohol and water vapours respectively. The outputs of each of the PDC are shown in Table1 and Fig. 3.4.

Table 1: Output of each of the sensors in different vapours

Porosity	Methanol	Ethanol	Iso-propyl Alcohol	Water
40	1.869	2.198	1.911	1.743
55	2.767	2.753	2.496	2.101
65	2.281	2.344	1.723	2.235
75	2.465	2.304	1.699	3.030

Fig. 3.4 (a) shows the response of the PS array for isopropyl vapor for the variation of concentration from 0 to 1200 ppm. Fig. 3.4 (b) and (c) show the response of array for ethanol and methanol vapors. Results as shown in Fig. 3.4 indicates that sensor 1 in the array has very small sensitivity for the low concentration of isopropyl alcohol but both the sensors 2 and 3

have significant sensitivity to isopropyl alcohol. Sensor 2 and sensor 3 exhibit the higher sensitivity for ethanol and methanol respectively.

To obtain the response curves of the array in presence of mixtures of three vapors like methanol ethanol and isopropyl alcohol again total mixture concentrations were fixed at 1000 ppm. The mixture vapors were formed adding three vapors in different proportions.

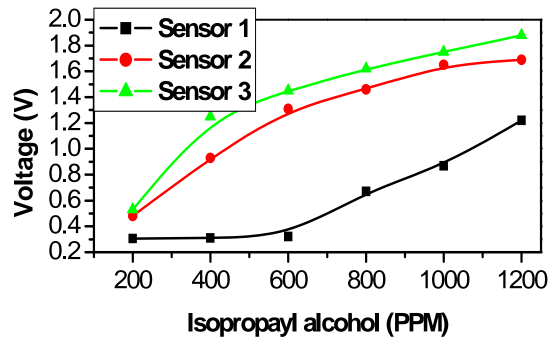


Fig. 3.4(a)

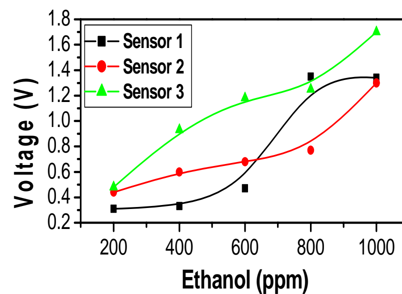


Fig. 3.4(b)

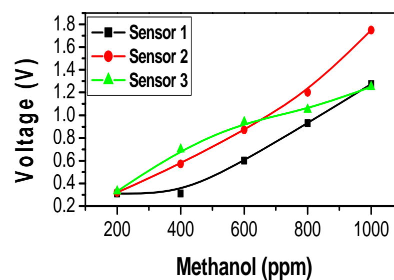


Fig.3.4(c)

Fig.3.4: Response of the PS sensor array for different\concentrations of (a) isopropyl alcohol (b) ethanol (c) methanol vapours.

Fig. 3.5 shows the dynamic response of the sensor 2 of the array for the mixture of the three vapors.

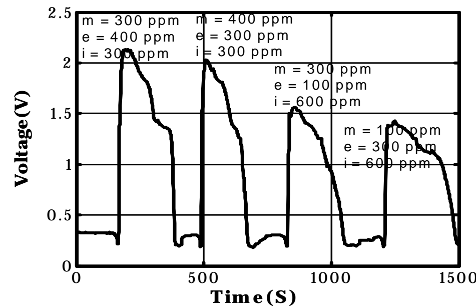


Fig.3.5 dynamic response of here vapours

4.Gas sensors

Porous silicon has been used as gas sensors, particularly for a number of gases like hydrogen,NO_2, CO etc

Hydrogen detection by porous silicon has been reported in [31]. The basic principle of operation of PS based hydrogen sensor is as follows:

Thin layer of Pd is deposited on the surface of the porous silicon layer consisting of silicon islands. As Pd on top of the high impedance PS layer adsorbs hydrogen, its volume expands bringing it in contact with neighboring Pd, dramatically reducing this impedance. The change in impedance is correlated to hydrogen concentration. The large surface to volume ratio in Pd nanoparticles in this sensor maximize the hydrogen adsorption area, while minimizing the diffusion of hydrogen due to reduced thickness of the particles.This results in higher sensitivity, faster response and shorter desorption times.

4.1 Hydrogen Sensor fabrication and Characterization[31].

The porous silicon layer was fabricated from a p-type (1 0 0) silicon wafer of low resistivity (0.001–0.004 ohmcm) by etching at a current density of 25 mA/cm2 for an hour. Pd is deposited by evaporation and annealed which oxidizes partly Pd to PdO. While the Pd directly absorbs hydrogen, PdO gets reduced by hydrogen and may return to Pd and contribute to the sensing of the hydrogen. Processes for the reduction of PdO to Pd takes place at 100^0C. The present sensor is operated at room temperature and the possibility of room temperature conversion is small. The sensors baseline resistivity was measured to be

2.20MohmcmThis large baseline resistivity opposed to that from the starting wafer is consistent with the formation of oxide and the porous nature of the substrate. The percentage change in resistivity as a function of hydrogen concentration in nitrogen is presented in Fig 4. The figure show that the sensor responds to concentration changes of hydrogen in real time both with increasing concentrations and decreasing concentrations. The porous Si template is the key to this stability and sensor performance. The porous Si template serves two purposes; it significantly increases the surface area for adsorption of the gas and simultaneously increases the baseline resistivity of the porous-Si film.

4.2 NO_2 Sensor [11]

NO_2 is a toxic gas whose concentration (100-200 ppb) determination in urban areas is becoming increasingly important but reliable and low cost NO_2detectors are not available. Porous Silicon based NO_2 at room temperature operation and low cost have been reported [11]. The molecules of NO_2 act as acceptors. Once they are adsorbed at the PS surface the acceptor like character would lead to increase of hole concentration resulting into an increase in conductivity. Sensor current depends strongly on relative humidity. An increase in RH leads to decrease in conductivity and sensor current. Water molecules behave as donor-like centres increasing the conductivity of PS. Fig. 4.2 depicts the dynamic response of the PS sensor to different concentrations of NO_2 in dry air.

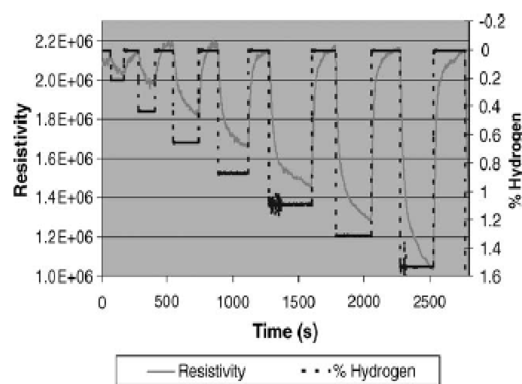


Fig. 4.1: Response of Pd- based sensor when percent hydrogen is initiated at 0.8% then decreased in four steps. Percent hydrogen is displayed in inverse order (scale on the right square steps) to highlight curve dependence at 300K.

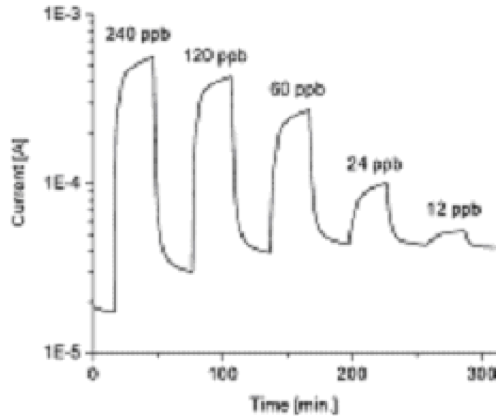


Fig. 4.2: Dynamic response of the sensor to different concentrations of NO_2 in dry air.

4.3 CO Sensor [12]

Photoluminiscence property of porous silicon can be utilised to detect many gases like CO, Methane etc at room temperature [12]. PL peak is observed to shift towards lower value as compared to that in air in presence of CO. Fig. 4.4 [12]. Porous silicon PS layers with 60% porosity and 80 mm thick were prepared from n-type silicon wafer. Plasma treatment in Argon and in Oxygen stabilizes electrical and optical properties of PS sensor.

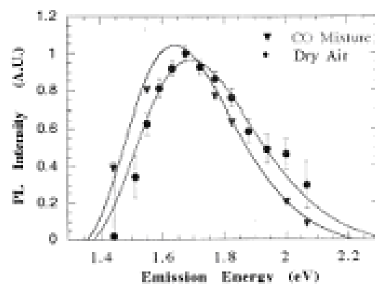


Fig. 4.3: Pl spectra of their best-fit v/s the emission energy in the range of 1.3-2.3 eV.

5 Pressure Sensor

NanoPorous Silicon being essentially nanocrystalline may have greater piezoresistivity than bulk monocrystalline silicon. This has been actually demonstrated in the laboratory. Further Youngs modulus of porous silicon is less than that of bulk silicon. Both these factors together lead to higher pressure sensitivity of porous silicon piezoresistor.[14]. Porous silicon pressure sensors are fabricated in the following manner. On a P-type monocrystalline silicon wafer

(100) of resistivity 1-3 ohm-cm, oxidation is done in a dry-wet –dry sequence to form a thick oxide (0.6 µm) layer. The sample is next micromachined by wet etchant at room temperature to the desired thickness. This is followed by porous silicon formation by anodic etching method in a two-pond cell. The area of the porous silicon layer is 2mm x 2mm.. Contacts on top of porous silicon layer are formed by vacuum evaporation of aluminium and its subsequent heat treatment at around 500°C for about 40-45 seconds. Contact area is 1mm x 1mm. The back contact metallisation is done by screen-printing of silver aluminium paste and its subsequent firing at 700°C for 45 secs. The thickness of the porous silicon layer has been restricted at 20µm on a p-type wafer since it has been found that on increasing the thickness further, the porosity increases and fabrication of ohmic and stable metal contacts becomes difficult. Thus the bulk silicon gives mechanical support to the structure. Also it provides the desired porous silicon-silicon heterojunction needed for integrated temperature sensing and compensation. Fig. 5.1 through Fig. 5.5 displays the pressure sensitivity of PS pressure sensors.

Fig. 5.1 displays typical pressure sensitivity of porous silicon piezoresistors. It is observed that the pressure sensitivity of nanoporous silicon pressur sensors is about three times that of bulk silicon. The sensitivity is also a function of porosity and is highest for a porosity of 55% (Fig. 5.2)

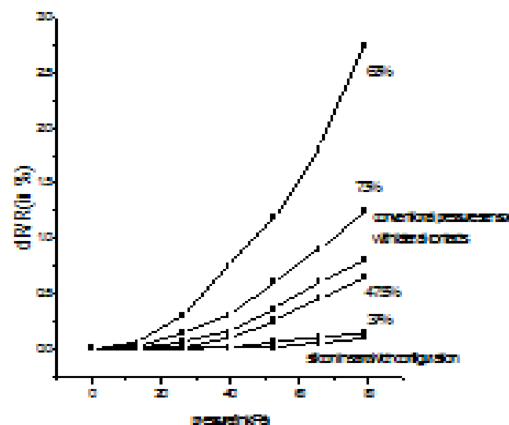


Fig. 5.1: Pressure Sensitivity of PS pressure sensors.

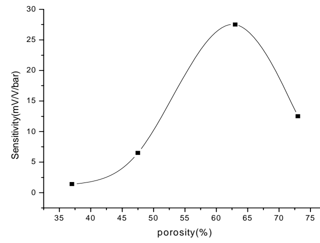


Fig.5.2

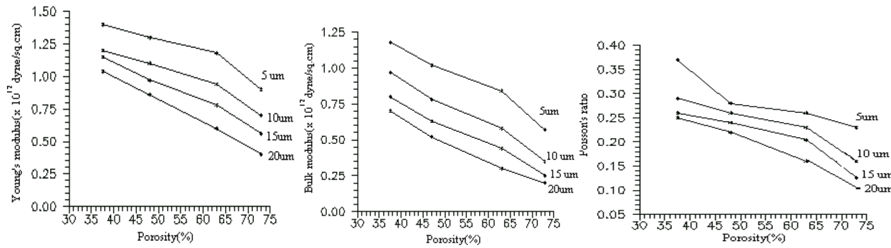


Fig.5.3: Young's modulus, Bulk modulus and Poisson's ratio of nanoporous silicon.

Variation of Young's modulus, bulk modulus and Poisson's ratio of a composite membrane for different thickness and porosity of porous silicon are shown in Fig. 5.3

The increase in the piezoresistivity of porous silicon with the reducing size of the silicon nanocrystallites is computed using deformation potential concept and is displayed in the Fig.5.4.

The increase in pezorsistivity of nanocrystalline silicon can be explained from the band structure of the quantum well structure of silicon. [15]. Fig. 5.5 shows that the piezoresistive coefficient increases significantly with the decrease in crystal size below 5 nm.

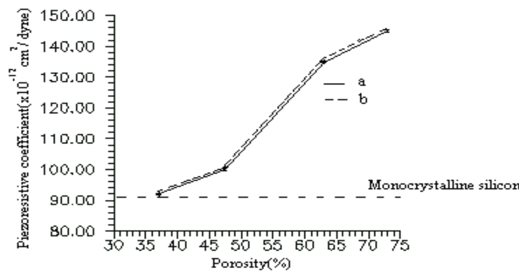


Fig. 5.4: Piezoresistive coefficient of nanoporous porous silicon with porosity.

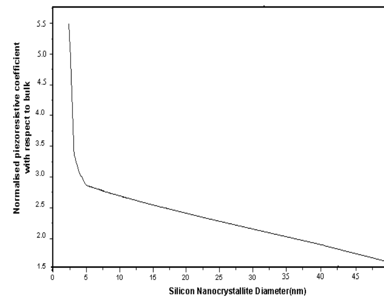


Fig. 5.5: Piezoresistive coefficient of nanoporous silicon with crystallite size.

6 BIO SENSORS

Biomedical measurements like the blood pressure, oxygen content, flow rate have been of great importance since the revolutionary work based on MEMS reported by Kendall Wise and his groups in 1979[32]. Today the medical invasive pressure measurements use fluid filled catheter that transfers measured pressure to external transducer [33]. However silicon being non-biocompatible, it has to be coated by some polymeric substance to render compatibility. But porous silicon has been reported to be biocompatible [34]. The first indication of its potential as a biomaterial has been proved by its reactivity towards hydroxyapatite formation [35]. Since then porous silicon has been used for various biosensing applications. Some preliminary experiments on the utility of porous silicon as sensors for DNA and proteins have been demonstrated based on light interference principles [36-38]. Porous silicon based microcavity resonators have also been used to detect gram (-) bacteria by properly functionalising the inner surface of a porous silicon layer with highly selective receptor molecules [39-43,20]. Such a structure translates the recognition of lipid A present in the bacterial cell walls into an optical signal. But these sensors are not yet able to distinguish between different types of gram (-) bacteria. Also these optical methods are expensive and lack the portability. There are reports of protein sensors binding wheat gliadin peptide using porous silicon based optical biosensor [44]. Recently, detection of DNA hybridization via a change in the conductance of mesoporous silicon layers have been demonstrated [17]. To realise a portable sensor using electrical detection technique, different contact geometries on such mesoporous silicon layer have been tried [46-49] but in almost all of them, the response of the device depends on the characteristics of the electrical contact with the porous silicon. To avoid this problem, contacts have been taken from the underlying bulk silicon [17] in a macroporous silicon sensor but that results in low sensitivity and high response time. We have

reported the use of macroporous silicon as a platform for electrical sensing of biochemical solutions where stable electrical contacts have been fabricated on porous silicon layer itself after oxidation both by thermal method and by hydrogen peroxide. The reason for using macroporous silicon as a platform is that it can be used to sense a wide variety of chemicals ranging from polar to organic molecules. The value of the capacitance of the sensor is found to be significantly large thus reducing the effects of parasitic capacitance in sensing. The capacitance can also be changed considerably by tailoring the dimensions of the lateral contacts on porous silicon layer. Macroporous silicon with such contact geometry also results in a very high change in capacitance on exposure to solvents which facilitates the design of the detection electronics. The solvents which have been used for sensing in this work are different concentrations of glucose, potassium chloride and sodium chloride. The sensor has been characterised in the presence of the biochemical solutions with both the different types of oxides. The porous silicon layer with thermally grown oxide shows a significant difference in response with solvents depending on their dielectric constant, dipole moment and molecular dimension.

6.1 Sensor fabrication

Porous silicon biosensors are fabricated by forming macroporous silicon as described in section 2.The porous layers are etched for 60 minutes resulting in about 30µm thick layers. The schematic of the sensor is shown in Fig.6.1.

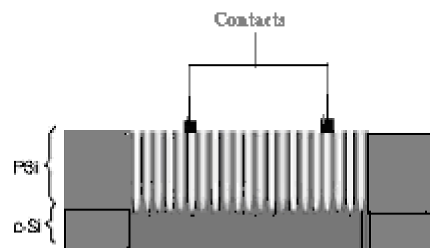
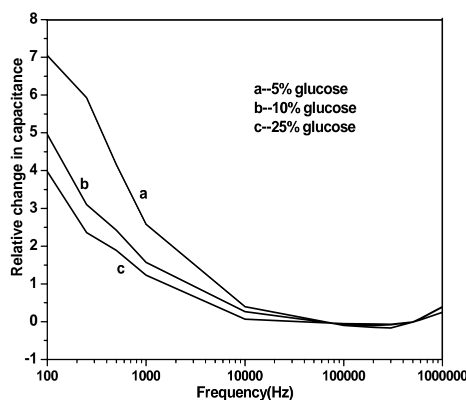


Fig.6.1 Schematic of the sensor

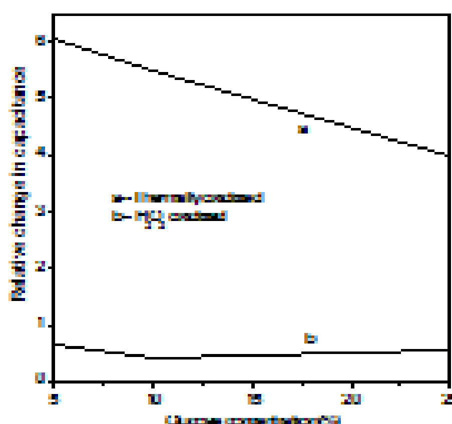
6.2 Measurement Results

The solutions used for measurement are 5%, 10% and 25% glucose solutions commercially available from dextrose anhydrous (Claris). 15% and 20% solutions have been prepared in the laboratory from 25% solution. The measurements have been taken upto 25% glucose since it is the highest concentration of commercially available monosacharride which is isomolar to

human plasma. Measurements have also been taken with potassium chloride solution available in the form of Potchlor solution (Claris). Each ml of the solution contains 150mg of potassium chloride. Five sets of solutions have been prepared by dilution with deionise water of 18MΩcm resistivity. The response of the sensor to glucose and water is shown in Fig.6.2 (a). Fig.6.2(b) shows the response of the H_2O_2 oxidized and thermally oxidized samples with different concentrations of glucose at a frequency of 100Hz. It is observed that the relative change in capacitance is more significant and linear for thermally oxidized sample in comparison to H_2O_2 oxidized sample. In thermally grown oxide, the change in capacitance is primarily dominated by the dielectric capacitance. The effect of the dipole capacitance is mostly screened by the thick thermally grown oxide.



(a)



(b)

Fig.6.2 (a) Variation of change in capacitance with and glucose concentration at a frequency of 100Hz frequency for different glucose concentration. (b) Response of H_2O_2 oxidised and thermally oxidised samples.

The response of the sensor with sodium chloride is shown in Fig.6.3 It is observed that there is a significant relative change in the capacitance of around 1800 at a frequency of 100Hz when exposed to a solution of potassium chloride containing 100mg in 1ml. The change in the capacitance decreases almost linearly in both the cases with decrease in concentration. The nature of the change can be attributed to the relatively high mobility of the potassium and sodium ions, which penetrates to a large extent within the pores affecting the space charge region at the silicon-silicon oxide interface.

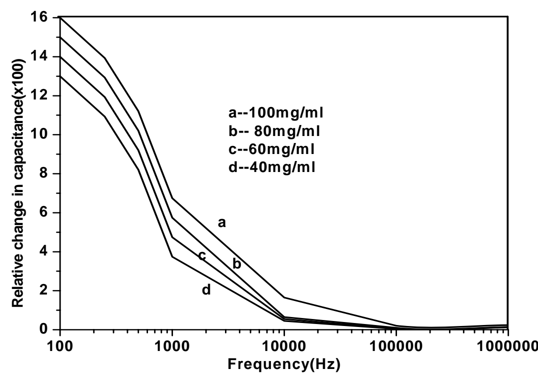


Fig.6.3 Variation of relative change capacitance with frequency for different NaCl concentration

Table 2

Sl no	Type of contact metal	W(cm)	d(cm)	Porous silicon sheet resistance under the metal contact r_{sc} (Ω/ □.)	Specific contact resistance r_c (Ω cm^2)
1	Nickel-copper	1	0.05	53.79	1.76 X 10^{-2}
2	Ag-Al paste	1	0.05	3.9K	2.06 X 10^{-1}
3	Aluminium	0.3	0.05	7.4K	1.92 X 10^{-1}

6.3 Challenges of PS sensor

It is to be noted that no commercial sensors based on porous silicon have been developed so far due to the lack of its stability and reproducibility. This is mainly because of the uncontrolled growth of pores on the silicon surface. Intensive research on ordered porous silicon formation by template transfer technology is required to apply the immense sensing potential of porous silicon commercial purposes.

(a) **Contact:** Making ohmic contact to any semiconductor is in general not so easy but for PS it is really a challenging task. The high resistivity (tens of kilo-ohms to tens of mega-ohms), presence of SiO_2 at the surface, doping difficulty , micropore to nanopore distribution and localised nonuniformity – all join together to realise ohmic contact on PS a real problem. Vacuum evaporation or sputtering of suitable metals followed by short heat treatments have not been always successful although most commonly practiced. Metal plating by electrochemical or electroless techniques need to be further improved. The problem is much more serious for p^+ PS. Most commonly contact is formed on PS layer by evaporating Aluminium and then annealing it subsequently. However Al contact usually is not ohmic in nature and displays rectifying characteristics. Further it undergoes ageing when exposed to atmosphere for a prolonged time. Low resistance contacts on porous silicon have been realized by electroless nickel deposition from a very weakly alkaline solution followed by copper thickening. Nickel is deposited over porous silicon by electroless deposition technique. 0.0038 M nickel sulphate solution is mixed with 0.242M ammonium fluoride solution at room temperature and PH adjusted to 7.5 Copper has been deposited over the nickel layer by electrochemical plating process to increase the metal layer thickness and to decrease the sheet resistance further. The specific contact resistance as measured by the above mentioned technique for three different metals like nickel, Ag-Al paste, aluminium with porous silicon is given in Table1.It is observed that the specific contact resistance for Nickel – copper plated porous silicon is better in comparison with other two. Similar values of contact resistance of silver on p-type silicon has been reported in [19]. Also on comparing the contact resistance of nickel on porous silicon with gold reported in [20] shows that contact resistance of nickel is around 10ohm while that of gold is around 20-100ohm.A low value of the sheet resistance for nickel compared to other metals is perhaps due to the formation of nickel silicide with porous silicon.

(b) **High Resistivity**: Porous Silicon is an effective media of Silicon, SiO_2 and void. The pore size and pore distribution and morphology as well as the volume fraction of Si/SiO_2 greatly affects the resistivity of PS. Besides a large number of traps and recombination centres are present at the Si/SiO_2 interfaces which capture the mobile carriers and increase the resistivity of PS very significantly. This is particularly important in p+ PS where a p+ Si attains a very high resistivity(>100 megohm-cm) after PS anodisation although the porosity is rather low (< 30%) . The probable quantum confinement of carriers in high porosity PS may contribute to its increased resistivity. Exposure to ambient and subsequent oxidation of Si changing the Si/SiO_2 volume fraction enhances the resistivity further. Metal, organic materials or polysilicon capping have been tried to prevent the oxidation caused by ambient exposure surface.

(c) **Non-uniformity**: It is well known that PS suffers from both vertical and lateral non-uniformity during its formation. This would lead to non-uniform distribution of resistivity, dielectric constant, refractive index and photoluminescence properties of PS which is undesirable for device functioning. Efforts to improve uniformity both vertical and lateral have been made by controlling the formation parameters and techniques but much more need to be done in this regard. Use of Alumina templates formed by depositing thin film of Al on silicon and then anodizing Al to form an ordered structure of Alumina may be tried for regular and ordered structure of PS. For removing vertical non-uniformity pore branching during formation of PS layer is to be avoided. Use of DMF based electrolyte solution during PS formation leads to vertical pores without pore branching. However the pore morphology is affected by the change of the composition of electrolyte, which needs to be optimisd for the purpose.

(d) **Doping Difficulty**: Doping of PS by thermal diffusion or ion implantation is rather difficult and very little work has been carried out in this regard. The presence of very high surface state density at Si/SiO2 interface, passivation of nano or micro-structured Silicon skeletons cause diffusion of desirable dopants rather difficult. Surface passivation of the pore walls by hydrogen treatment at high temperature are reported to lead to considerable reduction in surface state densities.

(e) **Instability**: One of the principal limitations of PS is its high surface activity leading to adsorption of moisture, oxygen and other contaminants in the ambient which subsequently change the composition of PS and cause its "aging". Lot of work has been done to prevent or

minimise aging of PS including capping of PS with metals, organic polymers and polysilicon. Oxidising PS intentionally right in the beginning is another approach for improving its stability. Oxidising of PS can be done by thermal oxidation, or by H_2O_2 treatment, or by anodic oxidation.

(f) **Local formation and patterning of PS**: For device fabrication it is essential to form locally porous silicon layers on a silicon substrate to a predefined pattern. This can be achieved in a number of ways: (a) by local anodisation of patterned crystalline Si surfaces through a mask, (b) selective anodisation using etch stops and (c) by patterning uniform PS through photolithographic and etching techniques. Lot of work needs to be done in this area. Attempts are being made to realize wheatstone bridge structure of PS piezoresistors for fabrication of a PS pressure sensor by lithographic technique.

(g) **Freestanding Porous Silicon**: Most of the PS devices are fabricated on PS/Si heterojunction but sometimes it is essential to have a freestanding PS layer. However the fabrication of freestanding PS and pasting on a suitable substrate with front and back contacts is still in aninfantile state. Freestanding PS layer has been fabricated in connection with solar cell fabrication but its use as sensors is yet to be explored.

7 Conclusions

Porous Silicon is an excellent platform for various types of sensors. Humidity sensors, Vapour sensors,Gas sensors,Pressure sensors and also BioSensors have been fabricated and tested in the laboratories. All of them have displayed very high sensitivity, room or relatively low temperature operation, desirable selectivity and also fast response time as compared to their conventional counterparts. Moreover porous silicon sensors are compatible to silicon IC technology. However their largescale commercial use has been prevented due to a number of limitations. These limitations are not fundamental but need to be overcome through ingenous engineering. Intensive research is called for this purpose.

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