

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.

2.1 Nanoporous Silicon

On a p-type monocrystalline silicon wafer of resistivity 1-2 Ω cm, 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/cm² and 10-30 minutes respectively. A porosity (P) of around 40- 80% and a thickness (t) of 10-50 μ m 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.

2.2 Macroporous layer formation

For macro porous layer formation the porous silicon layers are fabricated by electrochemical etching of p-type silicon (ρ 10-20 Ω cm) under constant current conditions with a current density of 4mA/cm² 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 15-20 μ m 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.

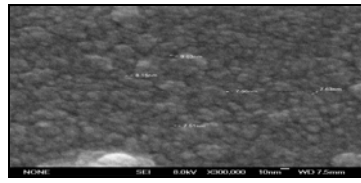


Fig.2.1 Nanoporous Structure

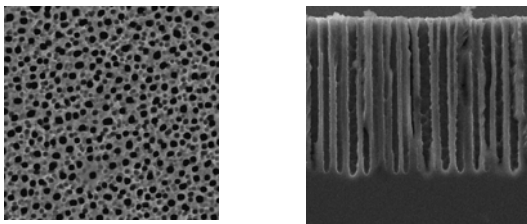


Fig.2.2 Macroporous structure

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.

3.1 Principle 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)

3.2 Fabrication 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.

3.3 Principle 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].

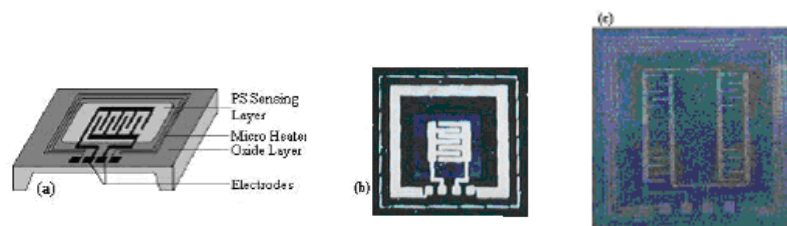


Fig. 3.1: a) Schematic and actual photograph of PS Humidity Sensor with (b) single PS layer and (c) four PS layers.

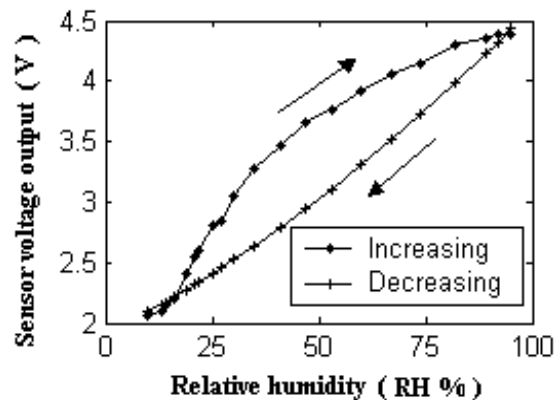


Fig 3.2: Response of porous silicon humidity sensor with the variation of humidity.

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.

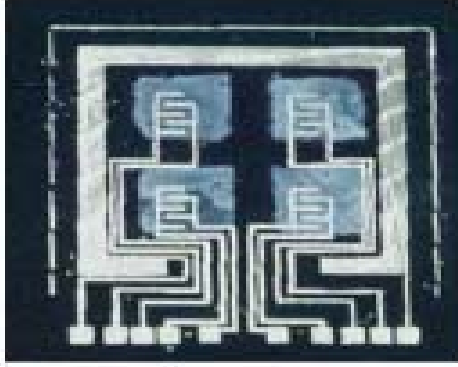


Fig. 3.3: Photograph (top view) of the PS transducer array.

3.4 Vapour 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 Table 1 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.

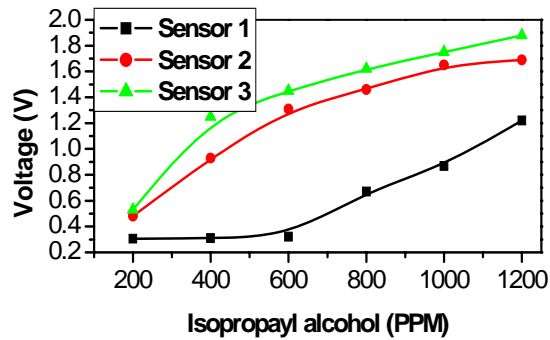


Fig. 3.4(a)

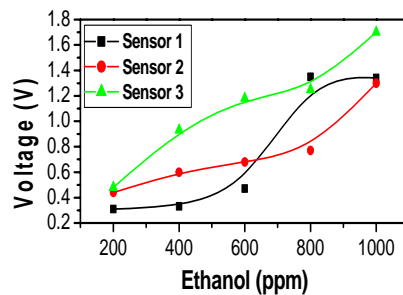


Fig. 3.4(b)

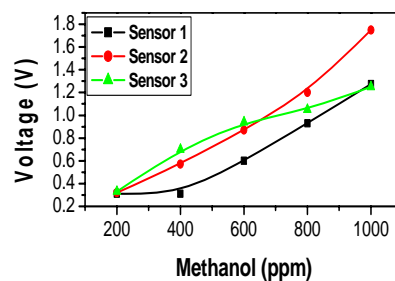


Fig.3.4(c)

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

2.20Mohmcm This 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 NO₂ Sensor [11]

NO₂ is a toxic gas whose concentration (100-200 ppb) determination in urban areas is becoming increasingly important but reliable and low cost NO₂ detectors are not available. Porous Silicon based NO₂ at room temperature operation and low cost have been reported [11]. The molecules of NO₂ 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 NO₂ in dry air.

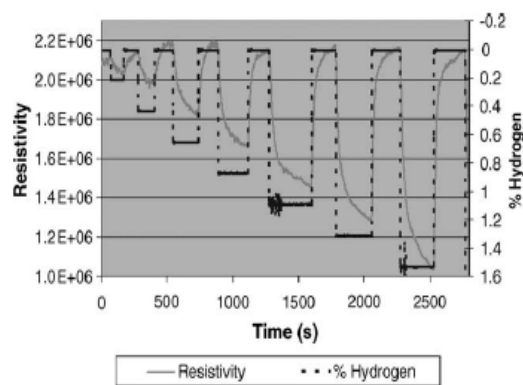


Fig. 4.1: Response of Pd- based sensor when percent hydrogen is initiated at 0.8% then decreased in four steps. Percent hydrogen is displayed in inverse order (scale on the right square steps) to highlight curve dependence at 300K.

(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 20 μm 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 pressure 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)

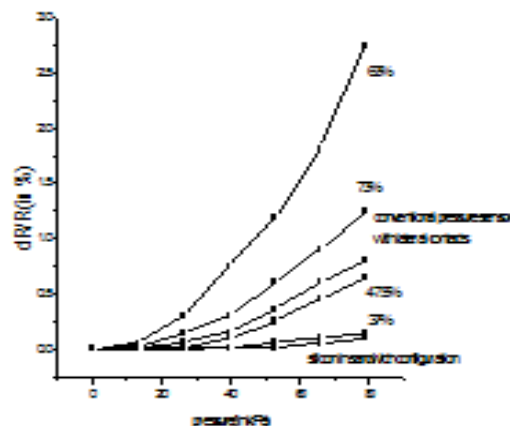


Fig. 5.1: Pressure Sensitivity of PS pressure sensors.

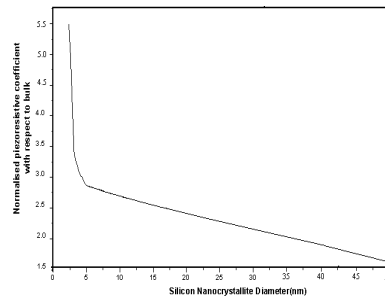
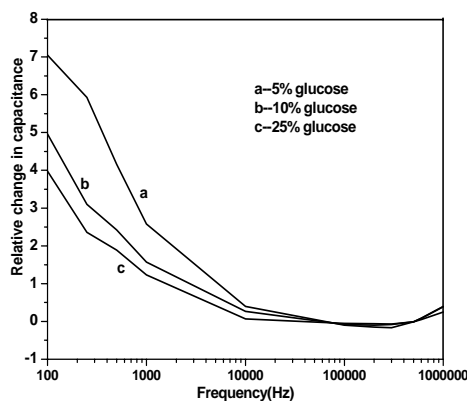


Fig. 5.5: Piezoresistive coefficient of nanoporous silicon with crystallite size.

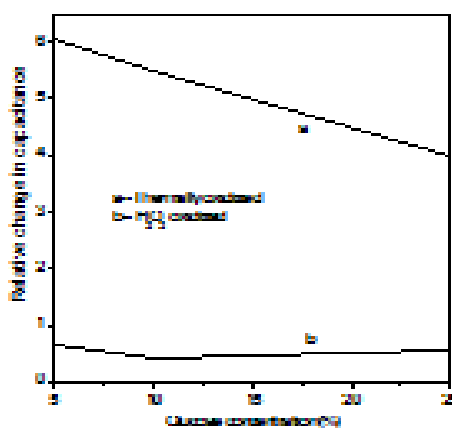
6 BIO SENSORS

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

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 $18M\Omega\text{cm}$ 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.

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 SiO₂ 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 Table 1. 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.

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 H₂O₂ 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 an infantile 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 ingenious engineering. Intensive research is called for this purpose.

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