CHAPTER – I

SEMICONDUCTOR OXIDE AND POROUS SILICON MATERIALS FOR GAS SENSOR APPLICATION

1.1 INTRODUCTION

In recent years, the search for smart sensors has stimulated microelectronics evolution with the development of new structures, materials and combination of processing techniques in order to obtain higher integration of transducers and signal processing capabilities. Silicon and silicon containing materials for electronic and optoelectronic device fabrication and catalytic silane and siloxane production form the basis for important technologies [1-6].

The possibility of basing the semiconductor industry on silicon alone by use of silicon based optoelectronic devices is appealing. However, the design and construction of light emitting silicon devices remains visionary. Porous silicon, which has shown promise in providing this elusive light emitting material, has been studied extensively with regard to its light emitting, photoluminescence, capability [7-14]. However, information is needed detailing the porous silicon surface chemistry with organic solvents. Research into this surface chemistry is clearly warranted since the porous silicon used technologically will probably be subjected to cleaning procedures involving organic solvents.

In particular, porous silicon (PSi) obtained by anodic electrochemical etching of monocrystalline silicon in HF solutions, has been an interesting focus of study, due to its strong and visible photoluminescence, observed for the first time by Canham in 1990 [15]. PSi film formation depends on electron injection from the electrolyte that consumes holes in the c-Si surface. The hole concentration is an important parameter to control PSi formation.

In producing silicon (100)-based devices [1, 2] solvent cleaning and production procedures [16-19] and growth protocols [20-22] are employed. The effects of cleaning and production solvents on the silicon and on subsequently grown layers have not been widely studied. As silicon device fabrication techniques and requirements become more advanced and demanding, organic and aqueous solvents will be required to remove contaminants more efficiently. An important first step in moving toward these more advanced processes will be to determine the surface chemistry involved when these
solvents interact with Si (100). Preliminary work has commenced with the investigation of H2O. The primary focus has been to determine whether H2O adsorbs by a dissociative or a nondissociative pathway and to determine the thermal decomposition properties of the resulting Si-H and %-OH surface species [23-28]. The interaction of organic molecules, such as ethanol and methanol with Si (100), is less well studied [29, 30]. Ethanol decomposition on Si (100) appears to be one of the first few detailed studies to be completed for Si (100).

Besides that, other properties as its high surface area and its perspectives for optoelectronic applications have been the sources of the numerous investigations [31-35]. Selective PSi areas have been also used as sacrificial layer for micromachining structures [36]; however, patterning of PSi layers after the anodisation is not compatible with other microelectronics processes, selective areas must be defined before PSi formation. Silicon dioxide, silicon nitride or N-doped superficial layer have been used as alternatives for masking PSi regions on Si substrates [37, 38].

The appearance of PL only in the samples which have been chemically etched following crystallization indicates that, while the presence of crystallites is a necessary condition related to the quantum confinement effect, the surface chemistry of the crystallites plays a role in the PL efficiency. Having these two factors in mind, a variety of Si-based luminescent layers could be prepared, as the precursor material-crystalline or amorphous-should be chosen regarding the application aims.

It has been established that visible RT PL is emitted by all the annealed and etched films irrespective of the annealing times ≤ 120 min. PSi films prepared from the samples are stable, as there is no difference between the PL of the freshly prepared samples and those stored in air for few months. The obtained results demonstrate the feasibility of luminescent PSi from the p-type PSi structure.

Silicon-based light emitting systems have attracted attention because of technological applications. Despite intensive studies in the field, a unique model explaining the experimental observations is still lacking and the microscopic processes involved in the luminescence are still a subject of debate [39]. It has been established that the PL spectra of these films are stable during several months of exposure to air [40]. Therefore, the study of PSi prepared from the deposited crystalline silicon is interesting because of both fundamental and application reasons. Using such a technological approach it is possible to study the effect of crystallinity of PSi on their photoluminescence spectra.
In the present work, semiconductor oxide materials like SnO$_2$ and ZnO have been chosen to be incorporated into the PSi structure, which may provide a large surface area heterostructures like SnO$_2$/PSi and ZnO/PSi fabricated for sensing hazardous gases with high sensitivity.

Oxide monolayer has the advantage of stabilizing the texture of PSi against heat treatment at higher temperatures. As long as no reducing atmosphere is used, heating of the layer can be performed for hours up to 900 °C, without any major changes in the porous texture [41]. This is clearly demonstrated when comparing the pore size distribution of the as formed layer to that obtained for the same sample, oxidized for two hours at 300 °C, and heated at 800 °C under vacuum for one hour. Consequently, when such a low-temperature oxidation is performed ('preoxidation'), the porous texture is stabilized and oxidation can be studied under reproducible conditions [42]. From oxidation kinetic result it clearly appears that complete oxidation of the layer is achieved only if the temperature is above 750 °C. Although oxidation always occurs throughout the whole porous volume, the temperature has to be high enough to allow complete oxidation of the pore walls.

For temperatures higher than 400 °C, under vacuum, coarsening of the porous texture occurs, and drastically increases with temperature. After heating at 900 °C, large voids of about 1 µm can be formed in the material, surrounded by thick silicon walls and the specific surface is dramatically decreased by more than a factor of 10. Hence, it is advantageous to use SnO$_2$ or ZnO oxide formation into the pores without reducing the surface area. Further, treatment of these sol-gel coatings at about 400 – 500 °C is sufficient to make oxides inside the pores, walls and silicon pillar, which can be used for making SnO$_2$/PSi and ZnO/PSi heterostructures for sensor application.

1.2 SILICON SINGLE CRYSTAL

The discovery of the unique electronic properties of silicon and the development of silicon has been one of the most important technical events of this century. While the electronic technology was being developed, technologists realized that silicon has also very interesting mechanical properties. The physical properties of silicon are shown in Table 1.1. It is a very durable and elastic material. When the methods for microstructuring which have been developed for microelectronics are applied, very fine mechanical structures can be produced [43]. The combined use of mechanical and electrical properties of silicon was applied toward the development of pressure and gas sensors. Further
development gradually introduced other physical phenomena like thermodynamics, optics, magnetism and hydrodynamics to the microstructure world. Nowadays there are silicon sensors for almost all conceivable quantities. The trend is to combine several sensors and actors together with electronics on one sample in order to get a full microsystem.

Silicon is a mono atomic semiconductor. It crystallizes in the cubic diamond lattice with $5.2 \times 10^{22}$ atoms/cm$^3$, the nearest neighbor separation being 2.35 Å and lattice constant 5.431 Å. It has a high melting point 1,420 °C. Relatively pure silicon with an impurity content of one or two parts per 1000 can be made by reduction of silicon tetra chlorate with Zn. This material can be then further purified by melting in vacuum and crystallizing. By slowly cooling the molten silicon down to room temperature good quality single crystal can be obtained with different orientations [44].

### Table 1.1

**Material properties of Silicon**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Gray</td>
</tr>
<tr>
<td>Type</td>
<td>p &amp; n-type</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>1.11</td>
</tr>
<tr>
<td>Structure</td>
<td>Cubic, diamond lattice</td>
</tr>
<tr>
<td>Space group</td>
<td>Fd3m</td>
</tr>
<tr>
<td>Lattice parameter (a) Å</td>
<td>5.431</td>
</tr>
<tr>
<td>Density (gm/cm$^3$)</td>
<td>2.3</td>
</tr>
<tr>
<td>Atomic density (cm$^{-3}$)</td>
<td>$5 \times 10^{22}$</td>
</tr>
<tr>
<td>Yield Strength (Breaking) (MPa)</td>
<td>1000</td>
</tr>
<tr>
<td>Yield Strength (Recommended value for Layout) (MPa)</td>
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</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>160</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>1414</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>2355</td>
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<tr>
<td>Thermal conductivity (W mK$^{-1}$)</td>
<td>150</td>
</tr>
<tr>
<td>Thermal expansion (K$^{-1}$)</td>
<td>$2.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Thermoelectric coefficient c-Si (µVK$^{-1}$)</td>
<td>800 – 1100</td>
</tr>
</tbody>
</table>
1.3 STRUCTURE OF SILICON LATTICE

The three dimensional silicon structure and the associated parameters are shown in Fig. 1.1. By adding small amounts of impurities called dopant to semiconductor crystals, it is possible to choose the dominant type of conduction in materials (either electrons or holes). When the conduction is due to impurities, the material is called an extrinsic semiconductor. The physical arrangement of added impurities, pentavalent phosphorous to a two-dimensional silicon crystal is given in Fig. 1.2. Qualitative dependence of the Fermi energy on the temperature and doping level of the impurity is shown in Fig. 1.3. As the temperature increases, more and more acceptor sites get filled or all the donor electrons get excited to the conduction band. At this state the material will approach its intrinsic characteristics with Fermi energy approaching the middle of the forbidden energy gap.

1.4 ENERGY BAND STRUCTURE OF SILICON

The band structure of silicon is shown in Fig. 1.4. The top of the valance band lies at $K=0$ and the energy surface are approximately spherical. The band is degenerate and the different curvature of the two energy surfaces correspond to the two types of holes with different mobilities. For slow holes, cyclotron resonance data gives a mass of $0.46 m_0 - 0.56 m_0$, depending on the crystal direction and for the fast holes $0.16 m_0$. There is also a third surface which is slightly separated (~0.03 eV) due to spin orbit splitting.

The lowest point in the conduction band does not occur at $K=0$, but some where along the (100) crystal direction. The energy surfaces are six equivalent ellipsoids, for which the effective mass along the transverse mode is $m_T = 0.19 m_0$. This surface is not degenerate and the average effective mass is $0.26 m_0$. Values close to these average values for holes and electrons have been estimated from the long wavelength reflectivity of p and n type silicon.

The minimum separation between conduction band and valance band, which is the thermal activation energy, is $1.08 \text{ eV}$ corresponding to an indirect transition. But, as seen from Fig. 1.4, the direct transition bandgap representing the minimum vertical transition is $\sim 2.5 \text{ eV}$. Such a direct transition will thus only be possible with visible photons and any IR absorption must arise from indirect transition [44].
1.5 GENERALITIES AND DEFINITIONS OF POROUS SILICON (PSi)

Porous silicon (PSi) was discovered by Uhlir in 1956 [45], when performing electrochemical etching of silicon. In 1990, Canham [15] showed that certain PSi materials can have large photoluminescence (PL) efficiency at room temperature in the visible region giving surprising result, since the PL efficiency of bulk silicon (Si) is very low, due to its indirect energy band gap and short non-radiative lifetime. The reason for this was the partial dissolution of silicon, which causes (i) the formation of small silicon nanocrystals in the PSi material, (ii) the reduction of the effective refractive index of PSi with respect to silicon, and hence an increased light extraction efficiency from PSi and (iii) the spatial confinement of the excited carriers in small silicon regions where non-radiative recombination centers are mostly absent. In general, PSi is an interconnected network of air holes (pores) in Si. PSi is classified according to the pore diameter, which can vary from a few nanometers to a few microns depending on the formation parameters. According to the general classification of porous materials, three size regimes are defined as: (1) Microporous (pore width \( \leq 2 \) nm), (2) Magaporous (2 – 50 nm) and (3) Macroporous (> 50 nm).

The word nanoporous is sometimes used for smallest-pore regime to emphasize the nanometric dimension. The volumetric fraction of air of the material is called porosity (P). The internal surface of PSi per unit volume can be very large, the order 500 m\(^2\)/cm\(^3\). The enhanced photoluminescence efficiency of PSi – compared to Si – has motivated research towards development of other porous semiconductor materials also.

1.6 FABRICATION AND STRUCTURE OF POROUS SILICON

The porous silicon described in this thesis was fabricated by the electrochemical anodisation of silicon in a hydrofluoric acid (HF) based electrolyte. This is the most common method of fabricating porous silicon though the use of an ammonium fluoride based electrolyte has also been reported [46-48]. The fabrication is usually conducted in the dark to prevent photogenerated currents contributing to the formation process.

An alternative method for fabrication is by a chemical strain etch [49] that requires dipping the silicon substrate in a hydrofluoric acid : nitric acid : water solution for 3-15 minutes. The porous silicon fabricated using this method is, however, inhomogeneous in both porosity and thickness due to the fact that hydrogen gas evolved during fabrication remains on the surface of the wafer.
For anodization, a silicon wafer is inserted into an etching cell (Fig. 1.5). The cell is filled with an electrolyte of HF and ethanol. The wafer in the middle is contacted with two platinum electrodes and a current is induced. The positive potential is applied on the backside and the negative potential on the front of the silicon wafer, where the porous layer is generated. The chemical reaction dissolving silicon is described as follows [50]:

\[
Si + 2HF + \lambda h^+ \rightarrow SiF_{2} + 2H^+ + (2 - \lambda)e^- \\
SiF_{2} + 2HF \rightarrow SiF_4 + H_2 \\
SiF_4 + 2HF \rightarrow H_2SiF_6
\]

For the chemical reaction, positive charge carriers are necessary. In p-type silicon, enough holes are available; for n-type, silicon holes are minority carriers and can be generated by illumination of the silicon. By using of anodization, porous silicon layer thickness up to 100 μm are possible.

For all porous silicon generation methods different fabrication parameters influence the pore dimensions and porosities, firstly the substrate doping level and the kind of doping, n- or p-type. In order to enable an etch process, n-type silicon porosification needs illumination for hole generation. The pore dimensions depend on the doping level as well, in most cases highly doped substrates create finer pores with lower porosity.

Secondly, is the concentration of HF used as part of the electrolyte. Lower HF concentrations get larger pores, the parasitic oxide will be removed slower, the pore diameter enlarges and the porosity increases. For anodization, the applied voltage resulting in a given current density, is an important factor. The electrolyte composition is one important fabrication parameter for well defined porous layers. The pore dimensions and porosity change with different ratios of HF and ethanol. HF is used for the dissolution of the silicon, i.e. the parasitic oxide in order to create pores. If the HF concentration in the etching solution decreases, the dimension of the pores increases and therewith, the porosity of the porous layer increases as well. Pores dimensions mean the diameter of the pores and remaining silicon skeleton. High HF concentrations remove parasitic oxide fast, and resulting in more smaller adjacent pores.

The another element of the electrolyte is ethanol in order to reduce the surface tension of the solution (also used for anodization). Surface wetting is important for good pore uniformity. The wetting agent ethanol is a factor of pore fitness. By increasing the
ethanol concentration, finer pores and a better uniformity of the porous layer are achieved.

1.6.1 Pore Formation and Bandgap Widening

The electrochemical anodization of silicon will only provide porous silicon if the supply of holes to the silicon substrate is the rate-limiting step. Figure 1.6 illustrates the chemical dissolution mechanism suggested by Lehmann et al [51, 52].

Once exposed to an air ambient, however, this surface changes to an oxide contaminated surface, the major contaminants being mainly those elements that occur in the air in gaseous form [53, 54]. Lehmann and Gosele [51] expanded their model by suggesting that, providing the current density remains below Jps, the pore formation is self-limited by the availability of holes within the silicon branches. For p-type silicon substrates under anodic bias, the limitation of the hole supply may be caused by quantum confinement. Figure 1.7 [52], shows the proposed band structure at the silicon – porous silicon interface. It is initially assumed that the pore walls are depleted of the holes necessary for the dissolution. If a hole in the silicon substrate has sufficient energy it can penetrate into the silicon branch causing additional dissolution and a further increase in the band gap. Holes will continue to penetrate into the branches until the band gap has increased sufficiently to prevent further migration of holes into the branches, limiting the dissolution to the bulk silicon - pore interface. Increased dissolution of the branches (increased porosity) is observed as the current density is increased due to the additional energy, the increased current density gives to the hole.

1.6.2 PSi Microstructure and Optical Nature

The crystal lattice of original silicon remains unchanged but it is somewhat expanded [55], and filled with grid or pores and cavities. Under visual inspection, the face of PSi is smooth and mirror-like with blue gray or golden brown colour. State of porous silicon is characterized by a parameter called 'porosity', i.e. the ratio of empty volume (volume of the pores) to the total volume of the sample porous layer, as well as the average size of the microstructure elements. The pore form, depending on crystallographic orientation of a silicon wafer, and also the type and quantity of a dopant, can be column type or represent a structure such as a coral or sponge type [56-58]. Depending on a size range of pores, the following classification of PSi layers [59] is made: microporous ($d_{por} < 2$ nm), mesoporous ($2 < d_{por} < 50$ nm) and macroporous ($d_{por} > 50$ nm) as shown in Fig. 1.8 a, b and c respectively. The pores merge among themselves
with the increase of porosity (Fig. 1.8 c), forming columns of single-crystal silicon of diameter of the order 2 to 5 nm [58]. These silicon columns, which later received the name 'quantum wires' [15], consist, in turn, of spherical or other form silicon clusters of nanometric size [58, 59]. The energy gap of PSi, being changed typically from 1.5 to 1.8 eV [51], is a function of the quantum wire (silicon) diameter. The silicon wire diameter depends on conditions of PSi formation processes and provides opportunity to vary band gap of this silicon. Just due to formation of quantum wires, transformation of the energy spectrum of single-crystal Si takes place and it converts from indirect bandgap semiconductor into the direct bandgap one and also enlarge the bandgap of silicon (1.11 eV) to a maximum of about 1.8 eV as shown in Fig. 1.9.

1.6.3 PSi Band Diagram for Photoluminescence (PL)

It should be obvious to assume that photoluminescence (PL) intensity is proportional to the number of electrons present in the initial energy state (from which the transition takes place) and the number of vacancies of electrons (holes) in the final state to which the transition takes place. For simplicity, we also assume that the PL is observed because of the radiative recombination of confined holes in valance band with the electrons at the bottom of the conduction band, which is always filled at room temperature and in presence of the exciting light of higher energy than the band gap of silicon. That is, the origin of PL lies in the recombination of photo generated excess electrons with the confined holes (in case of p-type sample) in the valance band of a well (Fig. 1.10). Now, if the state in the neighboring well of same energy (as that of hole) is filled then the electron can tunnel to the vacant state in presence of radiative recombination centres. The energy barrier faced by such an electron is \((h\nu - E_g)\), where \(h\nu\) is the energy difference between the lowest conduction band level and the energy level of the hole and \(E_g\) is the bandgap energy of bulk silicon. As we have assumed that the PL intensity is proportional to the number of vacancies in the valance band, the PL intensity \(W\) in presence of electric field should be \(W_o (1 - T)\), where \(W_o\) is the PL intensity in absence of electric field and \(T\) is the tunneling probability of such electron through a parabolic barrier [60].

1.6.4 The Physical Reason for Different Etching Rates and Chosing (100) Oriented Single Crystal Silicon Wafer

Some of the crystal planes etch fast, some very slowly. What is the physical reason for this phenomenon? To answer this question, we have to take a look at the silicon atom
(Fig. 1.11 b) and at the structure of a silicon crystal (Fig. 1.11 a). A silicon atom has four valence electrons. Since these repel each other, the electronic configuration has the form of a tetraeder as shown in Fig. 1.11 b, known as sp$^3$ hybridization. In a crystal, each of the four orbitals will be a covalent bond to another silicon. Therefore, the crystallographic structure for silicon has to contain tetraeders.

The crystal structure of silicon is a double cubic face centered lattice known as diamond structure shown in Fig. 1.11 a. First look at the empty spheres: they form a face centered cubic lattice. This structure has tetraeders in it and thus is able to house the geometry shown in Fig. 1.11 a, the figure has to be supplemented by the shaded spheres, which form a second face centered grating added to the first one to form the complete diamond lattice.

The crystallographic planes of a cubic crystal are shown in Fig. 1.12. The (100) plane is identical to a surface plane of the cubic. It has a four-fold symmetry, (110) is normal to the diagonal of a surface plane, it has a two-fold symmetry. The (111) plane is the normal to a volume diagonal, the symmetry is three fold.

Now let us consider the etching of a (100) plane. The direction of the etching attack is indicated by the arrow. The top layer is already removed as shown in Fig. 1.11 c. The black atoms are exposed to the etchant. These atoms have two bonds to the remaining crystal, the other two atoms is used to be connected to the already removed. Thus, for removing the atom, the etchant has to break two bonds. The situation of the single crystal atom is shown in Fig. 1.11 d.

The etching of a (111) plane gives very different view. Again, the black atoms are attacked by the etchant. Only one of their four bonds is removed with these atoms. The other three are still bound to the silicon crystal. This way, the atoms at (111) are far better connected to the crystal than the atoms at (100) surfaces. The situation of the single atom (Fig. 1.11 f) shows that we find one open bond versus three remaining ones.

The etching reaction described above is able to break two bonds simultaneously, but not three. When a chemical radical is attached to open bond, the crystal interatomic bond energy of the marginal atoms is changed [61]. Two OH$^-$ ions which are linked to the two free bonds of the silicon atom at the (100) plane will change the shape of the orbitals of the silicon atom by electrostatic interaction. This way they weaken the remaining bonds in a way that they can break easily. The plane etches fast. The effect on one OH$^-$ on the three bonds remaining at an atom of a (111) plane is much smaller. It does not weaken the bonds and thus the (111) etches slowly.
1.7 APPLICATION OF POROUS SILICON IN GAS SENSOR TECHNOLOGY

Porous silicon is a promising material for gas sensing mainly due to the substantially large surface to volume ratio and strong adsorption for gases [62]. Additionally, it is easy to fabricate with an advantage of controlling the surface morphology through the variation of the formation parameters. Most importantly, PSi is compatible with silicon integration technology [63]. Khoshnevis et al studied the effect of the anodization parameters during PSi formation on the sensor response for oxygen [64].

Beside the tin-dioxide the porous silicon is one of the most often mentioned materials in connection with gas sensor technology. The first group of application fields is passive application, when the PSi acts as heat isolator or sacrificial layer in the hot plate technology. Miniaturised hot plates are very important parts of pellistor and resistor type gas sensors, as the power consumption of these devices can be as low as several milliwatts at several hundred centigrade surface temperature [65, 66]. The heat conductivity of the PSi is lower than the c-silicon, which is the basis of its application as heat isolator layer. Also, the porous structure results in a very high surface to volume ratio, thus the sacrificial PSi layer can be etched away quickly and perfectly. The low power consumption and the short thermal transient time are remarkable advantages of thermally isolated micro hotplates.

The second group of application fields is the active application, when PSi acts as gas sensor layer with electrical or other (optical, thermal) readout possibility. There is an inadequate reflex, a wrong instinct, among scientists dealing with semiconductor gas sensors: “we need porous material for gas sensing…” and “porous materials are always good for gas sensing.” In some cases, when the total amount of adsorbed material is the basis of sensor operation, these statements have a strong basis. Capacitive humidity sensors [67] and PSi chemical sensors with optical detection (readout) [68] are the best examples. However, especially in the case of resistor type semiconductor gas sensor, what we really need is high surface/volume ratio, which can be fulfilled easily by thin layers as well. On the other hand, there is nothing to do with an extremely high specific area porous material, if its Fermi-level is pinned, as it is suggested in [69] and [70, 71] for the case of porous silicon. This is one possible reason for the fact that there is a huge number of articles dealing with PSi chemical and biosensors, but only a very few dealing with resistor type gas sensors. Seals and Gole [72] introduced a PSi gas sensor for detection of HCl, NH₃, and NO at the 10 ppm level. Their resistor type sensor operates,
but even authors themselves declare that “the full mechanism of response is a topic of continuing study”. There is some effort to explain the gas sensitivity of the PSi–Si layered structure with parallel electrodes on the top [70]. The current paths and electrode distance effects are discussed too. A very few similar PSi–Si structures are introduced as resistor type ethanol [73], NO₂ [74], organic vapour [75] and H₂ [76] sensors. There are no full explanations of the operation and theoretical basis of these sensors. Recently Luongo et al [77] reported about a Pd doped PSi, as a resistor type sensor for H₂ at room temperature. The authors state that the basis of this sensor operation is the volume change of the Pd particles dispersed on porous silicon layer, reducing the layer impedance due to closer contact with each other.

A field-effect transistor like structure has been realised by Barillaro et al. The porous floating silicon gate is located over a crystalline resistor [78]. The floating gate controls the resistor value modulating the interface potential barrier below. The advantage of this structure is that the PSi resistance is not involved in the measurement, thus contact problems are eliminated. There are some contact free methods to measure surface and interface potentials and potential barriers: vibrating capacitor (Kelvin) and surface photovoltage (SPV) measurements. The vibrating capacitor has long been used for investigating semiconductor gas sensor surfaces. This simple and exact method is sensitive to the contact potential difference (CPD) between a vibrating reference electrode and the surface to be investigated. There is a charge on these electrodes and an electric field between them due to the contact potential difference. This electric field is detected by measuring an alternating current produced by the vibrating reference electrode. If the contact potential difference is compensated by an additional voltage source, this charge and this field disappear and so does the alternating current. In this situation the CPD is equal to the compensating voltage. Optical excitation of the sample can be performed using a transparent conductor layer on a quartz plate as a reference electrode. Using this arrangement, the surface photovoltage (SPV) can also be investigated, and the interface potential barrier can be separated from the total potential change [79].

The surface photovoltage (interface potential barrier in the case of strong excitation) can be measured by a fix transparent reference electrode with chopped light excitation too. This arrangement can be completely contact free with capacitive coupling, while the vibrating capacitor needs a contact at least at the backside to keep the reference potential at fix value. There is only one attempt presented in the literature to use PSi–Si
structure as a sensor structure together with vibrating capacitor readout [80]. However, the authors say: “a palladium thickness of 20 nm was chosen in order to totally cover the porous surface”. In that case, their results are characteristic only on Pd surface and there is no evidence of the importance of PSi layer, as the vibrating capacitor is sensitive only to the work function change, and the continuous Pd layer completely shadows the potentials in the layers below. An alcohol sensor is presented in [81] with amorphous-silicon on silicon structure, which is somewhat similar to the PSi–Si system. The effect of ethanol adsorption on a-silicon was measured by the vibrating capacitor. The charge, the surface and interface potentials of the PSi–Si system were investigated by the vibrating capacitor (in thermal equilibrium and in presence of strong light excitation) and by SPV (static capacitor with chopped light excitation) [79]. The charge in the porous Si layer can be calculated from the interface potential barrier map. The p+ silicon is depleted or inverted below the thick porous Si layers; this reveals a large amount of positive charges in the porous Si layer. The steady state is a consequence of the equilibrium between the charge tunnelling out from crystalline semiconductor and trapping in the PSi, and charge tunnelling back from the PSi to the crystalline semiconductor.

Catalytically active noble metal particle doped PSi–Si structures have been investigated for aspects of gas sensing purposes using the same arrangement [82]. Some reversible CPD (contact potential difference) responses on H2 and ethanol vapour have been found at about 100 °C temperatures. The PSi layer is thin and transparent in the case of moderate metal doping, thus the PSi–Si interface can be excited separately. This makes it possible to measure the interface potential barrier change in the Si substrate, and calculate the change in the space charge layer from the general solution of the Poisson equation [79, 85]. This change should be equal to the adsorption induced change of the charge in the PSi layer. That theoretical possibility has not been used until now for calculation of charge related to adsorption/absorption. Instability is the most important problem related to the porous silicon. As a chemically active high surface/volume ratio material it can be oxidised easily. This is the chemical type instability. The macroporous, mesoporous or microporous PSi layers can be bare, partially oxidised, when Si domains are embedded into oxide matrix, or fully oxidised. There are a lot of different variations with strongly different physical properties, and these properties may change during the ageing (oxidation) process. However, the oxidised PSi may be more stable, and may contain less interface states effecting the Fermi-level pinning. The oxygen adsorption may result in conductance increasing too.
1.7.1 Importance of miniaturized solid state gas sensors

The demand for better environmental control and safety has increased research activities of solid-state gas sensors. Toxic gases have caused major accidents during the past several decades. Simple gas sensors are needed in order to sense the presence of such gases. Among these, CO is one of the most important, and the detection of CO by a simple device is an important research area [84]. While tin oxide (SnO₂) and zinc oxide (ZnO) have been used as materials for sensing reducing gases, many have attempted to develop gas-sensor materials with improved sensitivity and selectivity. The selective detection of CO in the presence of H₂, however, is very difficult, because the working mechanism of SnO₂ and other ceramic gas-sensing materials is based on the catalytic oxidation of gas molecules. H₂ undergoes facile oxidation and, thus, most types of ceramic gas sensors are more sensitive to H₂ than to CO. In the field of agricultural and biotechnological processes as well as air conditioning systems or monitoring of exhaust gases, there is an increasing demand on CO₂-sensors. Environmental concerns have stirred up much interest in CO₂ exhaust from energy power plants. A large part of CO₂ emitted in the atmosphere originates from the combustion of fossil fuels, especially coal and petroleum. To reduce the CO₂ exhaust from flue gases, several methods of CO₂ separation have been proposed [85]. Various approaches have been proposed recently in order to simplify or miniaturize the detection system. They utilize materials such as electrolytes, organic polymers, and oxide ceramics. Besides electrochemical cells and infrared devices, solid-state sensors can be used for CO₂-detection [86].

The detection of O₃ is in the center of interest due to its physiological relevance. As the maximum permissible concentration for ozone is very low at 240 μg/m³ (= 100 ppb), gas sensors need a high sensitivity together with good selectivity in order to avoid disturbing reactions with other oxidizing gases [87]. Several studies have been carried out on developing NOₓ sensors using semiconducting metal oxides and organic layers. The aging and response reproducibility of the sensing devices based on organic layers are poor, whereas the semiconducting metal oxides sensors appear to be more suitable to NOₓ detection because of its durability in severe working conditions [79]. Liquid petroleum gas (LPG), widely used as fuel for industrial and domestic purposes, has often proved to be hazardous because of explosions caused by leaks. It is, therefore, important to develop good sensors for the detection of LPG [88]. Gas analysis of human expiration provides important information on the state and functioning of different human organs, decompensation of some pathologic states, or exacerbation of chronic diseases. For
example, a quantitative determination of O$_2$ and CO$_2$ in the expiration characterizes gas-interchange functions of the blood and lungs [89]. One of the important methods in medical diagnostics of diabetes, allowing performance of an adequate therapy is the determination of acetone (CH$_3$-CO-CH$_3$) concentration in the blood of a sick person. This is usually made with the help of paper indicators changing their color under contact with the urine of the sick man. This method has obvious shortcomings in the application; moreover, the constraint between concentrations of acetone in urine and in blood is of a more complex character than the correlation of those parameters in expiration and in blood because the blood directly participates in the gas-exchange.

Dissolved oxygen measurement is important for medical, chemical, and environmental analysis. Electrochemical oxygen sensors have been shown to be a powerful tool for this measurement. Microelectronic fabrication technology has made a considerable impact on the development of miniaturized electrochemical sensors. With this technology not only can the sensor be miniaturized, it can also be made at a low price through mass production. These tremendous features make it very suitable for use in the biomedical field, where the small size of the sensors enables implantation in tissue [90].

Early detection and localization of fire is an important problem of the day. Wide usage of synthetic materials leads to a large liberation of toxic gas species in the beginning stage of fire and proved to be fatal for the human population. The traditional fire prevention sensors are not very effective in this case. Some of them react only to high temperature, which are not high in the initial stage of fire, especially outside the site of origin of fire. As a result these sensors cannot signal in good time about the appearance of toxic gases [91]. It is well known that the toxic products of combustion/smoldering of the majority of materials are CO, CO$_2$, Cl$_2$, SO$_2$ and different kinds of hydrocarbons or chlorinated hydrocarbons, chemically active radicals, and so on. Relative amounts of the indicated toxic components differ in a wide range, depending on the kind of burning materials. This fact excludes the possibility of using any selective gas sensors sensitive to one of the toxic products of combustion. For the reliable detection of a fire, independently of combustible material, the gas sensors for alarm system on the contrary must be non-selective and sensitive to the majority of toxic gases liberated at the fire. Semiconductor-based gas sensors are effective devices for early fire prevention and may be developed on the basis of their selectivity. Humidity sensors are required for climate control; home appliances; video recorders; warehouses; manufacturing of paper, food, tobacco, and textiles; (humidity) control in IC packages, and numerous other industrial processes and
medical applications. Most humidity sensors are based on electrolytic cells, ceramic resistors, and capacitors [92].

1.8 TIN OXIDE (SnO₂) BASED SENSORS

SnO₂ is a very interesting n-type semiconductor because of their specific combined electrical, optical and chemical properties. SnO₂ in its pure form is a wide bandgap semiconductor. As an undoped binary oxide, when fully stoichiometric in oxygen, it is nonconducting. In a perfect tin oxide lattice, all the charge-carrying valence electrons are tightly bound to the tin and oxygen atoms. Since activation energy of 3.7 eV is required to lift the valence electrons up to the conduction band, the probability of spontaneously elevating one electron at room temperature is a negligibly small value of 3.85 x 10⁻⁶⁴. Since a typical film will have about 10²² atoms of tin per cm³, each having an electron which could be promoted, the carrier density in a pure undoped fully stoichiometric SnO₂ film is 3.85 x 10⁻⁴² per cm³ which is practically zero. In order to become appreciably conducting, the carrier density must be 10¹⁷ per cm³. However, the electrical conduction does result, in undoped SnO₂ films, due to the existence of point defects in native atoms which act as donors. This is achieved by the oxygen vacancies in the lattice that can leave two unbound electrons on a tin atom or by a tin atom that may be located in an interstitial site with its valence electrons not particularly bound to any other lattice points. The properties of SnO₂ are presented in Table 1.2.

Tin oxide serves as an important base material in a variety of conductance-type gas-sensing devices. Tin oxide is an n-type, wide-band-gap (E₉=3.6 eV) semiconductor with the rutile structure. The electrical conductivity of tin oxide results primarily from the existence of oxygen vacancies, which act as donors. The (110) surface of SnO₂ is energetically the most stable and the predominant crystal face found in polycrystalline samples [93]. SnO₂ crystallizes with tetragonal rutile structure with space group D₄h₁₄ [P4₂/mnm] [94]. The unit cell contains six atoms, two tin and four oxygen as shown in Fig. 1.13. Each tin atom is at the centre of six oxygen atoms placed approximately at the corners of a regular octahedron, and every oxygen atom is surrounded by three tin atoms approximately at the corners of an equilateral triangle. Thus, it is the structure of 6:3 coordination.
Table 1.2  
Material properties of SnO₂

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>White or gray</td>
</tr>
<tr>
<td>Type</td>
<td>n-type</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>Direct, 3.7</td>
</tr>
<tr>
<td>Structure</td>
<td>Tetragonal rutile</td>
</tr>
<tr>
<td>Space group</td>
<td>D₄th¹⁴ (P4₂/mmm)</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td></td>
</tr>
<tr>
<td>a = b</td>
<td>4.737 Å</td>
</tr>
<tr>
<td>c</td>
<td>3.185 Å</td>
</tr>
<tr>
<td>Electrical conductivity (ohm⁻¹cm⁻¹)</td>
<td>1200 – 1400</td>
</tr>
<tr>
<td>Electron mobility (cm²/Vs)</td>
<td>10 – 50</td>
</tr>
<tr>
<td>Carrier concentration (cm⁻³)</td>
<td>10¹⁷ - 10¹⁹</td>
</tr>
<tr>
<td>Effective mass of electron</td>
<td>0.17m₀</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>1630</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>1900</td>
</tr>
<tr>
<td>Density (gm/cm³)</td>
<td>6.95</td>
</tr>
<tr>
<td>Dielectric constant (ε)</td>
<td></td>
</tr>
<tr>
<td>Parallel to c-axis</td>
<td>9.0</td>
</tr>
<tr>
<td>Perpendicular to c-axis</td>
<td>14.5</td>
</tr>
<tr>
<td>Thermal expansion coefficient (°C⁻¹)</td>
<td>4.0 x 10⁻⁶</td>
</tr>
<tr>
<td>Electron affinity (χₑ, eV)</td>
<td>4.85</td>
</tr>
</tbody>
</table>

Among the different materials studied for gas-sensing applications SnO₂ dominated over all other metal oxides and is the most extensively studied. The gas-sensing properties of this material has been widely been reported in the literature. A well known advantage of this material includes its low cost and high sensitivities for different gas species. A large number of dopants in SnO₂ have been investigated to improve response times, temperature of operation, selectivity, and so on. The surface morphology has been characterized to explain the exactly observed results by many researchers. Sn has a stable SnO and SnO₂ oxide formations. In the pure form SnO₂ is a semiconductor, with a bandgap of 3.6 eV, and its gas-sensing properties are also recorded even in the non-stoichiometric form [95-97]. In an ionic picture, Sn²⁺ has a ⁵S₂ electron configuration. The natural growth faces of SnO₂ are mainly (110) and (100) surfaces. It is reported that the Sn ions on the perfect surface of SnO₂ are all in the nominal Sn⁴⁺ state, as in the bulk.
The conduction and valence bands do not appear to be bent at this surface, that is, surface in a flat-band state [98]. For this reason, the surface and the bulk exhibit same resistivity values. The surface (110) is thermodynamically a most stable one. The interesting defect properties of this surface arise because of the bridging of O ions, lying above the main surface plane. These O ions can be removed easily either by heating or by particle bombardment. When they are removed, the two electrons left behind occupy orbitals, a mixture of 5s and 5p, on surface Sn ions, converting them to Sn^{2+}. The gas detection principle is based on the conductance variation of the sensing element (made of SnO₂) depending on the surrounding gas atmosphere and the temperature of the element, thus permitting the detection of many pollutant gases at very low levels (ppm or ppb). In the intrinsic form this material is sensitive to many gaseous species, such as: H₂ (25 to 650 °C), C₂H₅OH (25 to 500 °C), CO (131 to 570 °C), NOₓ (131 to 525 °C), CH₄ (200 to 320 °C), SO₂ (200 to 500 °C), H₂S (300 to 450 °C) and CO₂ (450 to 500 °C). Not all fabrication processes are compatible to the development of integrated gas sensors. One has to carefully select the material choice and the gaseous species before opting for the sensor fabrication.

The gaseous species interact with the material surface and induce reversible and reproducible electric responses on their interaction. A chemical modification of the SnO₂ surface takes place depending on the partial or total interaction [99]. In the simple form the resistance of the material consists of three parts, that is, bulk resistance, surface resistance, and contact resistance between metal electrodes and the material. Upon exposure to the gaseous species the surface resistance of the material varies and it brings out an effective change in the electrical resistance of the sensing element. The overall change of the element will be substantial if the exposed film surface area is larger and the temperature of the element is maintained throughout its physical dimensions. The structure of SnO₂ material is basically polycrystalline in nature and grain-boundaries dominate the effective changes in resistance that take place [100].

However, generally recognized poor selectivity and low thermodynamic stability of these SnO₂ materials at elevated temperatures have given rise to the search for new active materials [101]. In the case of SnO, SnO₂, and SnO/SnO₂ the equilibrium pressures of oxygen are quite close and the corresponding lines overlap. A relatively high equilibrium oxygen pressure of SnO₂ is responsible for a degradation of their electrical properties on prolonged thermal treatment in reducing gas atmospheres.
In practical applications, several attempts are usually made to overcome their disadvantages, by, for example, using chromatographic columns to separate the components, by operating at different temperatures, by choosing different burning-in procedures, dopants, and measuring frequencies. Nano-particulate film of SnO$_2$ has recently been implemented in work function based field-effect transistor sensors to detect NO$_2$. This has been reported to bring down the temperature of operation to 130 °C with little impact of humidity on gas sensitivity [102]. There are numerous reports showing that the gas-sensing properties of a semiconducting sensor are greatly affected by the addition of certain additives such as In, Cd, B$_2$O$_3$, noble metals, or metal oxides. These additives are added to improve sensor sensitivity to a particular gas, to minimize cross-sensitivity to other gases, and to reduce temperature of operation. Such surface/bulk modification techniques can be useful for developing a sensor, which is highly selective, that is, sensitive only to a specific gas [103]. Catalytic metallic additives such as palladium or platinum are often used to improve the selectivity and to enhance the response of these tin oxide based gas sensors.

The physical and the gas-sensing properties clearly depend on the method of preparation and surface morphology of the film in use [104]. The doping of SnO$_2$ with Pt reduces, in particular, the optimum operating temperature for sensing CO gas. On the other hand, the doping of SnO$_2$ with trivalent additive favors the detection of oxidant gases [105]. By suitably selecting the dopant, the temperature of device operations can be adjusted to suit a specific application. As an example the ranges of device operation are: for H$_2$ (150 to 250 °C), CO (50 to 350 °C), CH$_4$ (200 to 250 °C), smoke (20 to 550 °C), NO$_x$ (200 to 400 °C), and C$_2$H$_5$OH (100 to 300 °C). Doping (or addition) of other oxide materials also influences the detection capabilities of SnO$_2$.

Mixed oxide compounds such as iso-structural solid solutions of SnO$_2$-TiO$_2$ seem to be promising candidates for gas detection. Complex oxide systems may benefit from the combination of the best sensing properties of their pure components. Despite numerous studies on crystallographic structure and thermodynamic properties of SnO$_2$-TiO$_2$, present knowledge of the material parameters seems to be rather limited [101]. The SnO$_2$ compatibility to the development of integrated sensors is a mixed one. Some show excellent matching to silicon process conditions, particularly in a thin-film form. Some combinations are useful for hybrid microcircuits as well. The material in combination with Pt and Pd appears to be a good choice. It remains to be seen whether micromachined
silicon structures along with the material properties of SnO₂ dominate as an integrated sensor in the near future.

1.9 ZINC OXIDE (ZnO) BASED SENSORS

ZnO is a direct band gap semiconductor with $E_g = 3.3$ eV. The band gap of ZnO can be tuned via divalent substitution on the cation site to produce heterostructures. Electron doping in nominally undoped ZnO has been attributed to Zn interstitials, oxygen vacancies, or hydrogen. The intrinsic defect levels that lead to n-type doping lie approximately 0.01-0.05 eV [106] below the conduction band. The optical properties of ZnO, studied using photoluminescence, photoconductivity, and absorption reflect the intrinsic direct band gap, a strongly bound exciton state, and gap states arising from point defects. A strong room temperature, near-band-edge UV photoluminescence peak at $\sim 3.2$ eV is attributed to an exciton state, as the exciton binding energy is on the order of 60 meV.

Recent improvements in the control of background conductivity of ZnO and demonstrations of p-type doping have intensified interest in this material for applications in UV light emitters [107], homo and hetero junction photodiodes [108, 109], transistor [110, 111] and metal-semiconductor-metal (MSM) structures [112]. ZnO has several potential advantages over GaN for some of these applications, including the commercial availability of bulk single crystals and a larger exciton binding energy ($\sim 60$ meV compared with $\sim 25$ meV for GaN) [113]. The latter property should translate to even brighter light emission than obtained with GaN photonics. ZnO is an abundant material, very cheap compared to fluorine-doped tin oxide, ITO and GaN and other TCO. Moreover the absorption edge of ZnO is in the UV region. So homojunction photodiodes and UV-detectors can possibly fabricated using ZnO like GaN. ZnO has more potential advantages and will be discussed later in this section.

Most of the group II-VI binary compound semiconductors crystallize in either cubic zinc-blende or hexagonal wurtzite structure where each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa [114]. This tetrahedral coordination is typical of $sp^3$ covalent bonding, but these materials also have a substantial ionic character. ZnO is a II-VI compound semiconductor whose ionicity resides at the borderline between covalent and ionic semiconductor. The crystal structures shared by ZnO are wurtzite, zinc blende, and rocksalt. At ambient conditions, the thermodynamically stable phase is wurtzite. The zinc-blende ZnO structure can be
stabilized only by growth on cubic substrates, and the rocksalt NaCl structure may be obtained at relatively high pressures.

The wurtzite structure has a hexagonal unit cell with two lattice parameters, $a$ and $c$, in the ratio of $c/a = \sqrt{8/3} = 1.633$ and belongs to the space group of $C^4_{6v}$ or $P6_3mc$. A schematic representation of the wurtzitic ZnO structure is shown in Fig. 1.14. The structure is composed of two interpenetrating hexagonal-close-packed hcp sublattices, each of which consists of one type of atom displaced with respect to each other along the three fold $c$-axis by the amount of $u = 3/8 = 0.375$ in an ideal wurtzite structure in fractional coordinates, the $u$ parameter is defined as the length of the bond parallel to the $c$ axis, in units of $c$. Each sublattice includes four atoms per unit cell and every atom of one kind group-II atom is surrounded by four atoms of the other kind group-VI, or vice versa, which are coordinated at the edges of a tetrahedron. In a real ZnO crystal, the wurtzite structure deviates from the ideal arrangement, by changing the $c/a$ ratio or the $u$ value. It should be pointed out that a strong correlation exists between the $c/a$ ratio and the $u$ parameter in that when the $c/a$ ratio decreases, the $u$ parameter increases in such a way that those four tetrahedral distances remain nearly constant through a distortion of tetrahedral angles due to long-range polar interactions.

The basic material parameters of ZnO are shown in Table 1.3. To realize any type of device technology, it is important to have control over the concentration of intentionally introduced impurities, called dopants, which are responsible for the electrical properties of ZnO. The dopants determine whether the current (and, ultimately, the information processed by the device) is carried by electrons or holes. In semiconducting oxides, it is generally possible to achieve one or other of these types, but not both. The dopants are also called shallow level impurities because they introduce energy levels close to one of the allowed energy bands in the material and are easily ionized as a result. There may also be unintentional impurities introduced during the growth of ZnO that have a deleterious effect on the properties of the material. These are called deep level defects or impurities and may be either elemental impurities arising from contamination of the growth environment or structural defects in the ZnO crystal lattice. These structural defects can be vacancies in the crystal structure, substitutional or interstitials.
### Table 1.3

<table>
<thead>
<tr>
<th>Material properties of ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Color</strong></td>
</tr>
<tr>
<td><strong>Type</strong></td>
</tr>
<tr>
<td><strong>Band gap (eV)</strong></td>
</tr>
<tr>
<td><strong>Structure</strong></td>
</tr>
<tr>
<td><strong>Space group</strong></td>
</tr>
</tbody>
</table>

**Lattice parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3.249 Å</td>
</tr>
<tr>
<td>c</td>
<td>5.206 Å</td>
</tr>
</tbody>
</table>

| **Electrical conductivity (ohm⁻¹cm⁻¹)** | 1100 – 1500 |
| **Electron mobility (cm²/Vs)**        | ~ 2000      |
| **Carrier concentration (cm⁻³)**      | 10¹⁵ - 10¹⁹ |
| **Effective mass of electron**        | 0.27m₀      |
| **Melting Point (°C)**                | 1975        |
| **Boiling Point (°C)**                | 2360        |
| **Density (gm/cm³)**                  | 5.606       |

**Dielectric constant (ε)**

<table>
<thead>
<tr>
<th>Direction</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parallel to c-axis</td>
<td>9.9</td>
</tr>
<tr>
<td>Perpendicular to c-axis</td>
<td>11</td>
</tr>
<tr>
<td><strong>Electron affinity (χ, eV)</strong></td>
<td>4.35</td>
</tr>
</tbody>
</table>

In both cases, they may introduce energy levels deep within the forbidden band gap of ZnO and act as traps for carriers in the material. These uncontrolled defects make it very difficult to obtain reproducible device performance and reliability. Using techniques such as pulsed laser deposition (PLD), molecular beam epitaxy (MBE), or sputtering, ZnO of reasonable quality can be deposited at lower growth temperatures than GaN. This leads to the possibility of transparent junctions on cheap substrates such as glass, with the potential to realize low-cost UV lasers or light-emitting diodes for high-density data storage systems, solid-state lighting (where white light is obtained from phosphors excited by blue or UV light-emitting diodes), secure communications, and biodetection.

Zinc oxides, particularly the ZnO phase, are the thoroughly studied post-transition-metal oxide, one of the popular materials for gas-sensing application next to tin oxides. Their use as a gas sensor, in which the surface conductivity changes in response
to adsorbed gases, made them an ideal candidate in the early days of surface science. Point defects on ZnO surfaces are extremely important in gas sensing as they produce very large changes in the surface conductivity. The changes occur at the surface of the grains as a result of charge transfer and band bending caused by the adsorbates. The dominant defects identified in these films are O vacancies. Heating the films to high temperatures generally creates these vacancies. These surface defects do not produce any new filled electronic states in the bandgap [98]. This is related to the range of stable oxidation states of Zn.

In the intrinsic range ZnO is sensitive to O₂, O₃, H₂, CO, and simple hydrocarbons. However, ZnO is known as a good sensing material to detect reducing gases such as H₂, CH₄, and CO. This material also suffers from long-term instability, sensitivity to ambient humidity, and poor selectivity. By adding certain impurities it is possible to bring down the lower temperature detection limit of detection to the range of 127 to 200 °C. By doping the material with noble metals or Al, In, Ga the ZnO shows good sensitivity to NH₃ and ammonia-based gaseous species [115, 116]. The popular application of ZnO is its hetero-structures with other material components. In order to examine the electrical characteristics of SnO₂(n)/ZnO(n) interface and investigate its advantages as a gas sensor, stable and reproducible hetero-contact samples were fabricated by pressing and co-firing a layer of ZnO powder onto a layer of SnO₂ powder. The resultant composite pellets maintained very stable contacts between SnO₂ and ZnO during the entire measurement procedure and thus reproducible data were obtained. The electrical characteristics of the SnO₂/ZnO hetero-contact interface were examined to explain the increased sensitivity of the hetero-contact sample to 200 ppm CO gas.

Composite type sensors were suggested to improve the reliability because they contain many hetero-contacts between two phases. For example, ZnO(n)/CuO(p) composite showed higher sensitivity to CO gas than pure ZnO. ZnO(n)/SnO₂(n) composite also showed enhanced sensitivity that was related to the SnO₂/ZnO grain boundary. However, because the electrical characteristics of composite are influenced by many factors, such as the volume fraction, grain size, and the geometric arrangement of each phase, it is difficult to isolate the influence of the heterogeneous grain boundaries between two phases. Ever since the hetero-contact of CuO(p)/ZnO(n) was proposed to show high selectivity for CO gas, many kinds of hetero contacts have been studied [117]. However, hetero-contact type sensors have poor reliability due to mechanical contact of two dissimilar materials. Application of hetero-contact allows the formation of p-n, n-n
junctions, and Schottky diode structures. From the compatibility point of view this is considered as a healthy sign for the silicon device fabrication scheme. Hybrid microcircuit technology is opted mainly because of well-developed screen-printing techniques for ZnO-based materials.

1.10 AIM OF THE PRESENT WORK

The principal aim of this thesis is to prepare SnO₂/PSi and ZnO/PSi heterostructure by the sol-gel spin coating technique and to characterize their structural, optical, electrical and morphological properties and to study their suitability for developing gas sensors.
REFERENCES


Fig. 1.1 Single crystal silicon structure
Fig. 1.2 Two dimensional silicon crystal
Fig. 1.3 Dependence of Fermi energy on the temperature and doping level of the impurity
Fig. 1.4 Band structure of silicon
Fig. 1.5 Schematic cross section of an etching cell used by anodization
Fig. 1.6 Suggested mechanism for the electrochemical dissolution of silicon

1. In the absence of electron holes, a hydrogen saturated silicon surface is virtually free from attack by fluoride ions in the HF based electrolyte. The induced polarisation between the hydrogen and silicon atoms is low because the electron affinity of hydrogen is about that of silicon.

2. If a hole reaches the surface, nucleophilic attack on an Si-H bond by a fluoride ion can occur and a Si-F bond is formed.

3. The Si-F bond causes a polarisation effect allowing a second fluorine ion to attack and replace the remaining hydrogen bond. Two hydrogen atoms can then combine, injecting an electron into the substrate.

4. The polarisation induced by the Si-F bonds reduces the electron density of the remaining Si-Si backbonds making them susceptible to attack by the HF in a manner such that the remaining silicon surface atoms are bonded to the hydrogen atoms.

5. The silicon tetrafluoride molecule reacts with the HF to form the highly stable SiF$_6^{2-}$ fluoroanion.

The surface returns to its 'neutral' state until another hole is made available.
Top left - schematic diagram for the formation of porous silicon

Top right - silicon branch isolated by two pores. Two possible ways for the hole to cross the silicon - porous silicon interface are shown (broken and dotted arrow).

Bottom - band diagram of the silicon - porous silicon interface and the two different energy barriers for the hole penetrating into the wall (broken arrow) or into the electrolyte (solid arrow)

Fig. 1.7 Band diagram of the silicon-porous silicon interfaces
Fig. 1.8 Ideal model of porous silicon structure with different porosity

(a) Porosity 25%

(b) Porosity 50%

(c) Porosity 75%
Fig. 1.9 Schematic energy diagram of the radiative recombination process for H-PSi and D-PSi

Fig. 1.10 Schematic of proposed band diagram of porous silicon and possible transition during photoluminescence
Fig. 1.11 Wet chemical anisotropic etching
Fig. 1.12 Crystallographic planes of the cubic lattice of silicon (a) (100) plane, (b) (110) plane and (c) (111) plane
Fig. 1.13 Tetragonal rutile structure of tin oxide (SnO₂)
Fig. 1.14 Wurtzite structure of zinc oxide (ZnO)