catalysts usually made of noble metals such as Pd, Pt, and so forth are used to increase sensitivity of such sensors. They also require temperature of 300–400°C for their operation and are affected by moisture content. These have low selectivity which is considered a disadvantage.

Zinc oxide

Zinc oxide crystal has hexagonal wurtzite form. It is made into n-type ceramic by doping with In (indium) and is then used to detect hydrocarbon gases. When platinum surrounds the n-type ZnO ceramic, it becomes specially sensitive to fuel gases such as isobutane and propane whereas using Pd as a catalyst, it may be made sensitive to H_2 and CO.

Materials of the kind Co_3O_4, WO_3, and Fe_2O_3 can also be similarly used for gas detection purposes.

When oxygen in air is chemically absorbed or 'chemiabsorbed' in metal oxides such as SnO_2 or ZnO, electrons become locally aligned at the surface that produces a negative surface potential and there a charge carrier depletion occurs. This means that the surface conductivity is low. This chemiabsorbed material when exposed to a gas, cause the gas to react with oxygen, decreasing the surface-bound oxygen as also the resistivity. The phenomenon is enhanced at an elevated temperature of a few hundred degrees when the reaction is rapid and also reversible. Figure 6.21 shows a typical arrangement of the sensor with heater.

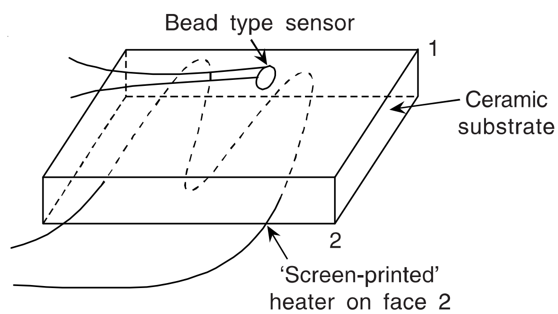

Fig. 6.21 A sensor using chemical absorption.

As mentioned already, Pd or Pt, or oxides and salts of noble metals increases the reactive selectivity as well as reactivity of different gases with oxygen. Selectivity and sensitivity are functions of temperature, peaking at specific values. This temperature dependence makes the sensors suitable for combustion monitoring purposes. They can be developed for a specific stoichiometric air-to-fuel ratio (λ) when a change of state is observed.

Titania (TiO_2)

Titania also forms a tetragonal rutile structure and is very useful as a flue gas monitoring sensor. Under reducing conditions, heating causes it to lose oxygen thus, generating oxygen vacancies which is then balanced by reducing Ti^{4+} to Ti^{3+}; and an electron donor situation arises. With increasing loss in oxygen with higher temperature, increasing number of electrons contribute to this conduction process and in the temperature range 300–1000°C, TiO_2 behaves as an n-type semiconductor. Other than temperature, partial pressure of oxygen also accounts for this conduction. Again, for TiO_2 with a Pt catalyst surface, oxygen mobility changes. If TiO_2 is porous, Pt coats a wall and sensitivity as well as response are high.

Pervoskites

Pervoskite structure is one structure in which materials such as $BaTiO_3$ can be found. It is cubic above Curie temperature (120°C). When temperature is brought below 120°C, spontaneous polarization takes place with all its Ti^{4+} ions shifting to O^{2-} ions and a permanent dipole moment is induced. The symmetry of the structure is now tetragonal making the polarized region ferroelectric. Below 5°C, the structure becomes orthorhombic which changes further below –80°C. All these changes in structure are reversible. If Ba^{2+} is replaced by Pb^{2+} or Sr^{2+}, the Curie temperature can be changed.

A special type of pervoskite is the $PbZrO_3$–$PbTiO_3$ called PZT family which is further modified by adding lanthanum, and is then called PLZT. PLZT is a solid solution but has a decreased ferroelectric stage, that is, lowered Curie temperature.

Varistors

These are ZnO based semiconductor devices and are used as electric field sensors. Above a certain value of applied field, which is breakdown value, they show large change in current flow for small voltage changes. The performance of the varistors are, to an extent, dependent on manufacturing processes. However, the conduction is through grain–grain interfaces. The details of operational mechanism are not very simple and are beyond the scope of present text.

6.10 CHEMFET

Chemically sensitive FET, in short ChemFET, is a specially designed FET which is adapted in IC technology with special encapsulation and packaging.

In a chemFET, the induced field is established by series combination of applied 'gate' potential and the interface potential due to chemical sensitivity of the 'source' or the substrate. The ordinary design is shown in Fig. 6.22. The stability of the system is ensured by coating it with silicon nitride. However, by depositing different electrochemically active materials on top of this silicon nitride layer, sensors for different ions can be obtained. Thus, aluminosilicate glass is used for sodium ions, valinomycin doped PVC may be used for potassium ions, and so forth.

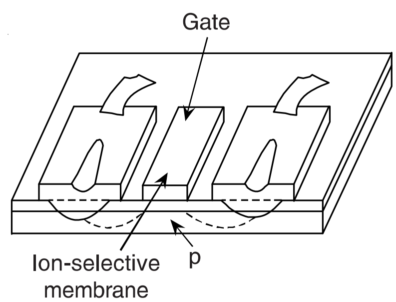

Fig. 6.22 A chemFET.

It must be remembered that for proper functioning, electrical isolation from the surrounding of the chemFET is essential. The active regions of the FET are isolated from the substrate by p-n junctions. A chemFET chip with polyimide mesh suspended over the gate region is sketched in Fig. 6.23.

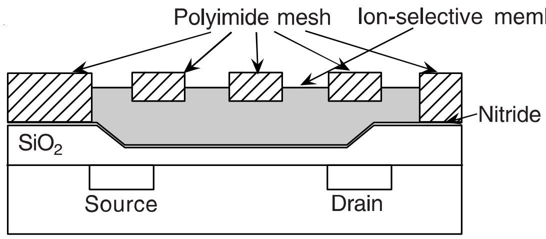

Fig. 6.23 The chemFET chip with polyimide mesh over the gate.

The main problem is the adhesion of the membrane to the FET. Well-shape was adopted for better adhesion, but the lifetime of this adhesion is still very short. A polyimide mesh was patterned over the active gate area and the mesh is 'asked' to entwine the solvent cast membrane and keep it anchored to the gate. For polymer gel, the problem is solved to a certain extent, but not for others, by selective deposition. The micromachined version shown in Fig. 6.24 solves this problem to a great extent.

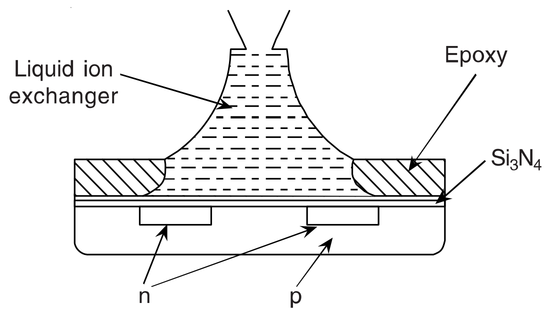

Fig. 6.24 Another version of the chemFET chip for polymer gel.

REVIEW QUESTIONS

1. Describe the basic construction and operation of an electrochemical cell. Define the terms—electrode potential, cell potential, and half-cell potential.

What is Nernst equation? How does it account for the cell potential of an electrochemical cell?

Calculate the potential for a half-cell consisting of Zn electrode immersed in a solution that is 0.030 M Zn^{2+}.

[*Hint:* The reaction indicates $Zn^{2+} + 2e \rightleftharpoons Zn(s)$ and from standard table, $E^0 = -0.763$ V, so that

$$E = E^0 - (0.0591/n)\log\{1/[Zn^{2+}]\}$$
$$= -0.763 - (0.0591/2)\log(1/0.03)$$
$$= -0.866 \text{ V}]$$

2. What is a standard hydrogen electrode? What is its utility in instrumental analysis?

What is a junction potential? On what factors, does it depend? Why often a salt bridge is necessary in sample analysis through electrochemical cells? What is its function?

3. How is cell potential affected by polarization? What are the different types of polarization? What are practical means of countering it?

4. Why is a reference electrode needed in a sample analysis? What are the commonly used reference electrodes? Write the functional state relations of a silver reference electrode and explain the meaning of these relations.

5. What different types of sensor electrodes are known to be used commercially? To which type the first, second, third kinds, and, redox types belong? How are they different—construction-wise and operation-wise?

6. Distinguish between the operations of ion-selective and molecular selective membranes.
What is selectivity coefficient of a membrane electrode?
How is boundary potential defined in a membrane electrode set up? Obtain an expression for the same.

7. Explain the action of a liquid ion exchanger membrane for generating a cell potential. What are the specific types of materials used for such membranes?
What is ion exchanger immobilized–in–polyvinylchloride membrane?

8. Show the constructional features of a gas-sensing electrode system using a gas-permeable membrane. What are the gases commonly detectable by such types of electrodes?
Indicate what internal solutions are required for (i) SO_2, (ii) NH_3, and (iii) CO_2. Write the functional state equations for SO_2 analysis.
What is an equilibrium constant? What is its function in solving for the output cell voltage?

9. Describe the special molecular selective electrode called biomembranes with due reference to materials, construction, functional state equations, and preservation.

10. Explain the characteristics of electroceramics such as ZrO_2, TiO_2, and (SiO_2, $ZrCr_2O_4$) and show how do they use their ionic conductivity, semiconductivity, and surface ionic conductivity respectively for measuring oxygen content and humidity.
Discuss on the recent developments of such electroceramics as gas sensors.