CHAPTER-II

CHAPTER - II

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2.1 Introduction

Now-a-days considerable interest has been developed among the research workers in converting solar energy into electrical or chemical energy by the use of solar cells.

A solar cell, being a device to convert solar energy into either electrical energy or chemical energy through photoelectric effect, requires a semiconducting material in the form of thin film. Thin films of semiconducting materials can be deposited by employing various conventional deposition techniques, namely, chemical vapour deposition /1/, Chemical bath deposition /2/, spray-pyrolysis /3/ and solution-gas interface technique /4/. The preparation of reliable, homogeneous and reproducible films by any of these methods requires knowledge of the interface.

2.2 Interface

Interface is defined as a boundary between two different materials or two grains of differing orientation of the same material. It plays an important role in all modern electronic devices, especially in solar cells. However, very little and scant knowledge is available about the interface. The reason for lack of experimental knowledge of interface is that interface phenomena occur in a few atomic layers buried under the numerous atomic layers of a bulk solid or liquid. In some cases, interfacial properties are dominated by a few atomic layers of impurities or defects that contain minute quantities of material when compared to the bulk /5/. Some interface properties are very sensitive to preparation techniques and a well-characterized sample

is, therefore, obtainable with difficulty /5/. The theory of interface is also not developed as this problem combines many of the most difficult areas of solid state physics. The structure of the interface remains unknown and the disorder may play an important role. Self consistent rearrangement of charge at the interface is important in shaping the properties and the atomic movement is crucial in affecting the interface. For these reasons much cf our knowledge about interface is empirical in nature /6/.

2.3 Types of Interfaces

Theoretically interface can be grouped mainly into the following seven categories, namely

i) Solid-Vacuum

ii) Solid-Gas

iii) Solid-Liquid

iv) Solid-Solid

v) Liquid-Vacuum (if no vaporisation takes place)

vi) Liquid-Liquid (if no mixing takes place) and

vii) Liquid-Gas Interface

(a clean surface is a solid-vacuum or a liquid-vacuum interface).

Over the last ten to fifteen years there has been so much progress in this field that it is not within the scope of this chapter to cover all the interfacial systems. Therefore, emphasis is given here only to the solution-gas interfacial system and also to some extent

solid-gas and solid-solution interfacial systems. Research on these three interfacial systems is highly promising, since phenomena of heterogeneous catalysis, surface reactions, double layer structure, surface adsorption, surface corrosion and many of the age old surface related problems may be better understood by studying these three systems. But even then a complete study of solid-vacuum and liquid-vacuum interfacial systems would encompase studying various properties like,

i) Surface composition and purity

ii) Surface thermodynamics and surface diffusion

iii) Electronic properties of clean surface and

iv) Interaction of photons with surfaces, etc.

Most of these properties are interrelated /7/. A model of heterogeneous system /7-11/ is considered in order to explain the interrelation between the solid-solution, solid-gas and solution-gas interfaces.

2.3.1 Solid-Gas Interface

There are two types of gas adsorption taking place on the surface of the solid, namely, physical adsorption (physiosorption) and chemical adsorption (chemisorption). The physiosorption results from the action of Vander Waals forces, which are considered to be made up of 'London dispersion forces' and classical electrostatic forces /7/. With these forces there is no transfer or sharing of electrons between a molecule and the solid. The binding energy is usually

less than 10 K Cals/mole. Further in physiosorption both adsorbate and the substrate suffer only minor distortions as a result of Vander Waals forces. In the chemisorption, on the other hand, electrons are shared or transferred between the adsorbate and the substrate. The binding energy is 10 K Cals/mole. The rate of bond breaking and the rate of new bond formation over a solid are the most essential steps in a heterogeneous (solid-gas) interfacial system. The role of surfaces is that the reactant must be chemisorbed for some time on the solid surfaces. For better reactivity, it has been found that the substrate should be a II -VI and V - VI compound and their alloys /7/.

An atom or molecule that approaches the surface of the solid always experiences a net attractive potential. As a result there is a finite probability that it is trapped on the surface. In usual terminology this probability is called the sticking coefficient which may vary between zero and one. Under the usual environmental conditions all solid surfaces are covered with a layer of adsorbed gas molecules or several layers of gaseous molecules. If the concentration of the gas molecules interacting with solid surface is more, then adsorption rate will be more. However, rate of adsorption decreases with increase in temperature. This is attributed to the thermal motion of gaseous ions or molecules which increases with temperature and results in decrease in adsorption. It is observed that at higher temperature the surface of the solid is clean and reflecting /11/. From these observations it is clear that at every temperature there is a different state of adsorption equilibria. These adsorbed layers of the gas molecules may form trap centres and affect the semiconducting properties of the solid.

2.3.2 Solid-Solution Interface

Many properties of the solid in contact with other materials cannot be explained adequately in terms of bulk properties. Much of this needed further knowledge of interface between solid and solution. There are widespread consequences of the fact that the surface of nearly all phases carry a net electric charge and form a one side of an electric double layer. Among all properties of the solid, solution interface aspect of surface forces is an important factor in knowing the interface structure of solid and solution. The principle theories were proposed by various authors to explain the double layer structure /12/. We have given a just outlook of the structure of the double layer. When a thin solid film is in contact with the solution carrying positive and negative ions, a charged double layer is formed at the interface, due to electro-static force of attraction between the ionic species of the solution and surface force of thin solid film. According to the electro-neutrality principle , the positive ions are attracted by the negative ions without net electron transfer to form a parallel plates of oppositely charged ions, the distance between these two ionic plates must be equal to the ionic radious of the respective ions.

According to Helmholtz and Parrin double layer theory an electric double layer is a flat plate condenser, one plate of which is directly connected to the solid wall and other plate carries opposite charge on solution side. The potential between these two plates apparently falls very sharply as shown in Fig. 2.1 and the value of surface charge (6') will be determined /11,13/

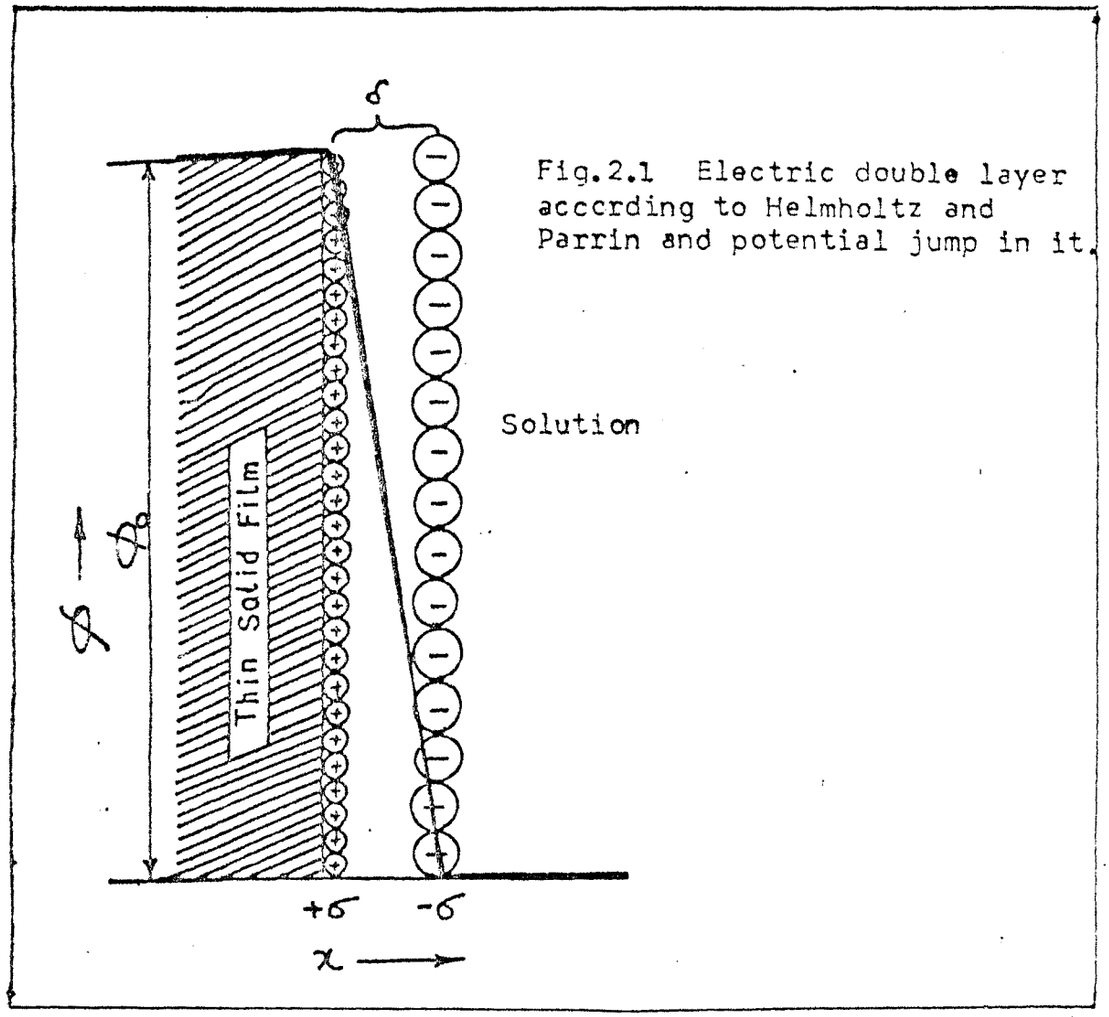

Fig.2.1 Electric double layer according to Helmholtz and Parrin and potential jump in it.

$$6' = \frac{\epsilon}{4\pi\delta} \quad \phi_o$$

where

ϵ = dielectric constant of medium,

ϕ_o = potential difference

δ = distance between two plates of the double layer denoted by + and - signs.

The absorption phenomena of the solid-solution interface is similar to that of solid-gas interface. Adsorption at the solid-solution interface is always complicated due to the solvent effect i.e. adsorption depends upon the medium in contact with the solid surface /14/. It is assumed that, higher the surface tension of the medium in contact with the solid, lower will be the adsorption, however, in non-aqueous medium having lower surface tension more will be the adsorption. Adsorption also depends on the time, temperature and the concentration of the solution.

2.3.3 Solution-Gas Interface

A gas molecule experiences an attractive potential up on approaching the oppositely charged solution surface. The strength of this attractive potential determines the affinity of gaseous ions towards the metal ions contained in the solution. Frequently the range of attraction of oppositely charged ions depend upon the distance between solution surface and the gas molecules. If the range of

force of attraction is short, then the interaction of the positive and negative ions of the gas and metal salt solution takes places /11,13-14/. If the distance of the gas source from the solution surface is increased, the solution surface experiences a weak interaction with the gas molecules. The electrostatic potential of the surface atoms of the solution involves a direct charge transfer with colliding gas molecules. Such a charge transfer interaction is of short range and leads to a formation of new molecule involving neutralisation of charges. The reaction of H_2S or NH_3 gases with the solution surface containing metal ions depends on the nature of solvent and pH of the solution.

Herrick et al /15/ studied the effect of gas on the surface tension and temperature of solution. According to their observations, surface tension of the solution decreases with increase in gas contact on the solution surface.

Ions on a surface of the solution are in an environment markedly different from the environment of the ions in the bulk of the solution. In view of the reaction at the interface, the ions at the surface of the solution are surrounded by favourable neighbours than the ions in the bulk. There is an aniotropic distribution of these neighbours near the solution surface. Gubbin and Thompson /16/ studied the molecular and density operation profile at the solution-gas interface. The molecular arrangement at the surface was given by Takahashi /17/. At the equilibrium condition ions tend to form the preferred orientation at the surface of the solution, however, the situation is different in bulk of the solution.

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The solution-gas interface can be further categorised as follows :

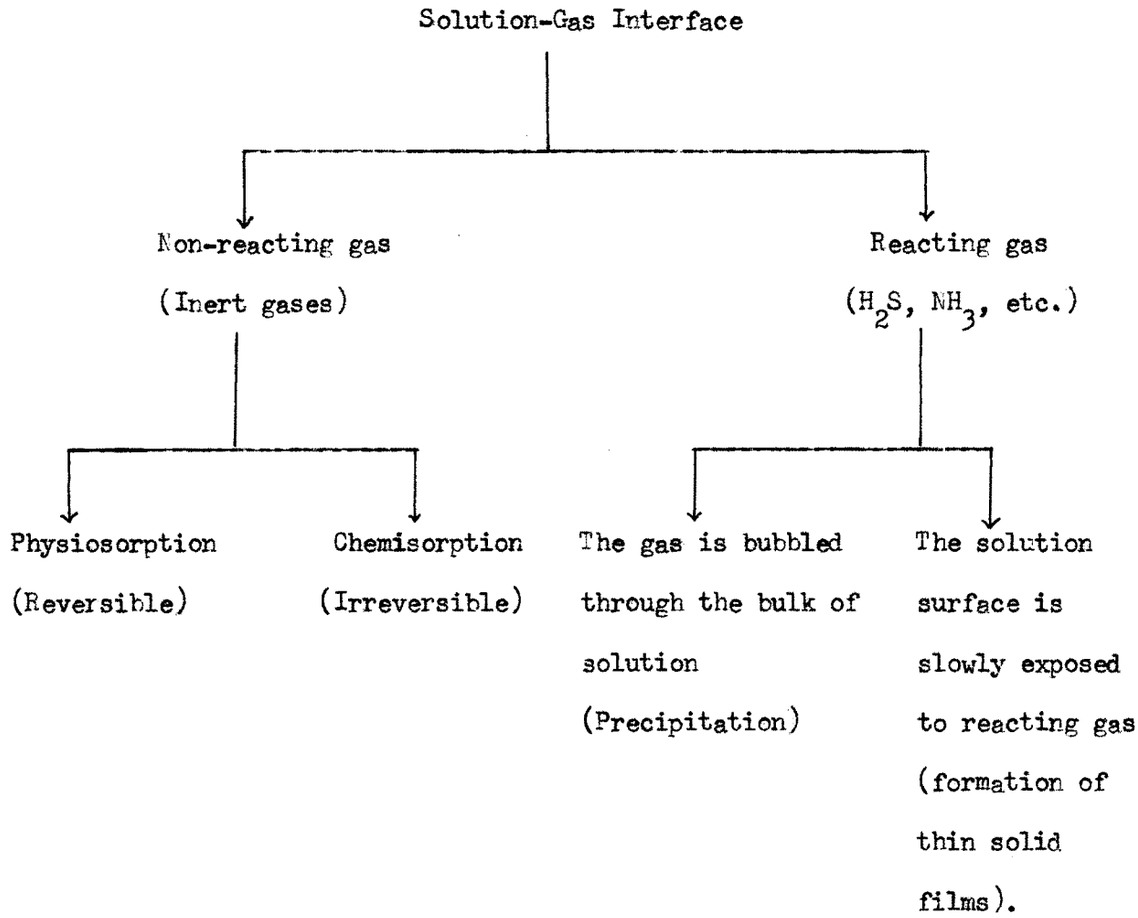

Fig. - Solution-Gas Interface.

The gases like H_2, CO, CO_2, N_2, CH_3 and all other inert gases do not react directly with the solution surface. These gases only get adsorbed on the solution surfaces. The adsorption of inert gases on solution surface may always be termed physiosorption on the basis of binding energy of the adsorbate which is very low (1-3 K Cals/mole)/7/.

1) Precipitation

When the reacting gas is bubbled through the bulk of solution precipitation occurs which depends upon various parameters, namely, solubility product, temperature, composition of the solution, solvent medium etc.

There are three types of precipitates, namely, crystalline, curdy and gelateneous. These differ only in their particle size. According to the Van Weimerns Rule /18/ the slow precipitation gives larger particles i.e. slow crystallization gives larger crystals, because ions or molecules require more time to rearrange themselves in an ordinary manner upon the faces of the crystals. However, in rapid crystallization ions or molecules have no time to arrange themselves on the crystal sites and hence the formation of new nuclei results and we get very small crystals. The speed of precipitation is greater when the solution concentration is high and it depends upon the solubility of the precipitate /18/.

$$\text{Speed of Precipitation} = K \frac{Q - S}{S}$$

Where Q = Momentary Concentration of the solution

S = Solubility

and K = Proportionality Constant.

The number 'Q-S' represents the force favouring the precipitation and denominator 'S' expresses an opposing force to the precipitation. The formation of solid phase from a solution involves two processes,

one of these is the nucleation and the other is the particle growth. The size of the particles of a solid phase is dependent on the relative rates at which these comp-eting processes take place.

II) Nucleation

For any precipitate there is some minimum number of ions or molecules required to produce a stable second phase particle in contact with the solution, called as nucleus. The formation of such nuclei is necessary for precipitate formation. The rate at which nuclei form in a solution is dependent on the degree of supersaturation. In highly supersaturated solution the velocity of nucleation increases rapidly. The rate of nucleation increases exponentially with the supersaturation as

$$\text{Rate of Nucleation} = K \ (Q - S)^{X}$$

where K and X are constant, X being greater than one. The number of nuclei come together to form stable particle, as

$$nA^{+} + nB^{-} = (AB)_{n}$$

where n is the minimum number of A^{+} and B^{-} ions that must combine to yield the stable particle $(AB)_{n}$.

III) Particle Growth

The second process that can occur during precipitation is the growth of particle due to coagulation. The growth can only begin when nuclei are present in the solution. In case of the ionic solid the process involves deposition of cation and anion on appro-

priate sites of the particles, which can be presented as /18/

$$(AB)_n + A^+ + B^- \quad (AB)_{n+1}$$

$$(AB)_{n+1} + A^+ + B^- \quad (AB)_{n+2}$$

The particle size can be increased by increasing the solubility of precipitate during the period of its formation, which can be done by carrying out the precipitation at elevated temperatures. According to above reaction if we consider the $(AB)_n$ is the particle and we want to increase its size then it is necessary to add cations and anions of the same compound in the solution mixture.

Secondly the particle size can be increased by coagulation process using colloidal solutions. Colloidal particles have a tendency to adhere to one another if brought into close contact. If the plane surface of the two particles come together, the positive ions of one could attract the negative ions of the other and vice-versa and a strong bond between the two particles would result.

Many precipitates become coarser when they are in contact with the mother liquor. During equilibration small particles disappear while materials from them is deposited on larger particles. This effect is known as Ostwald ripening /18/. The driving force causing this effect is called the surface energy and every surface boundary is associated with a certain amount of surface energy which is defined as /14/

$$S = \left(\frac{\partial F}{S_a} \right) T.P.$$

where, F is the free energy, Sa is the surface area, S is surface energy, P is a pressure and T is the temperature. The surface energy S is the same thing as the surface tension at liquid-gas or liquid-liquid interface. Thus any process is spontaneous which produces a decrease in surface energy at constant temperature. All surfaces tend to become as small as possible, this applies to the surface of solid precipitate. The solid can reduce its surface area by agreegating to form larger particles. The small particles have larger surface area than larger particles and the solid is rigid. The material from the smaller particles can go into the solution and redeposite on larger particles. Solubility product of smaller particles is higher than larger particles.

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R E F E R E N C E S

1 J.H. Kennedy and K.W. Frese, J. Electrochem. Soc. 123, 1683, (1976).

2 N.R. Pavaskar, C.A. Menzes and A.P.B. Sinha, J. Electrochem. Soc. 124, 5, 743, (1977).

3 S.H. Pawar and P.N. Bhosale, Mat. Chem. and Phys. 11, 462, (1984).

4 R.R. Chamberlin and J.S. Skarman, J. Electrochem. Soc. 113, i, 86, (1966).

5 H. Wilder, in proceeding of 5th Annual Conference on the Physics of Compounds Semiconductor interface, in J. Vac. Sci. Tech. 15, 5, (July/August 1978).

6 A. Heller, K.C. Chang and B. Miller in A. Heller Ed. 'Semiconductor-liquid solar cells' Inc. Princeton N.J. (1977).

7 B.C. Khanra, in 'Emerging Trends in Surfaces, Interfaces and Thin films' Ed. A.S. Nigvekar, A. Pimpale and P. Panat, Department of Physics, University of Poona P. 8-23, (1983).

8 S.H. Pawar and P.N. Bhosale, Mat. Chem. and Phys. 11, 461, (1984).

9 R.R. Chamberlin and J.S. Skarman, J. Electrochem. Soc 113, 82, (1966).

10 A.S. Baranski and W.R. Fawcett, J. Electrochem. Soc. 127, 766, (1980).

11 S.H. Pawar and P.N. Bhosale, in 'Emerging Trends in Surfaces, Interfaces and Thin Films', Ed. A.S. Nigvekar, A. Pimpale and P. Panat, Department of Physics, University of Poona P. 65-74 (1983).

12 J.O.M. Bockries and A.K.N. Reddy, Modern Electro-Chemistry Vol. 1,2, A. Plenum/Rosetta Edition, Chapt. 7,8 (1973).

13 S. Voyutsky 'Colloid Chemistry', Mir Publishers Mosco P. 90-200, (1978).

14 G.A. Somarajai, 'Principles of Surface Chemistry', Prentice Hall JNC, New Jersey P. 187-190, (1972).

15 C.S. Herrick and G.L. Gaines, J. Phys. Chem. 77, 2703, (1973).

16 K.E. Gubbins and S.M. Thompson, Farady Sym. Chem. Soc. (G.B.) 16, 59, (1981).

17 R. Takashash, Japan, J. Appl. Phys. 22, 17, (1983), and 21 17, (1983).

18 D.A. Skoog and D.M. West, 'Analytical Chemistry', Rinehart and Winston INC (N.Y.) P. 205, (1979).