CHAPTER I

CHAPTER - I

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1.1 Introduction :

The electronic properties of the transition metal dichalcogenides have been the subject of recent experimental as well as theoretical interest because of the wide range of electric and optical properties exhibited by these compounds. There is considerable current interest in establishing the electronic energy structure of those transition metal dichalcogenides which crystallise with layered structure[1]. Of this group of solids molybdenum disulphide is most extensively investigated. MoS_2 and WSe_2 belong to the class of transition metal (M) dichalcogenides, type MX_2 where $X = S$, Se or Te, which crystallize with a layer structure.

Further, considerable interest has been displaced in the use of semiconducting layer type transition metal dichalcogenides as photoelectrodes in the form of films, in electrochemical cells[2-8]. These investigations result from Tributsch's suggestion,[2-5] that these materials would be stable against photodecomposition under visible light while employed in an electrochemical solar cells. When these materials are exposed to visible light there result d-d band transitions, therefore, these materials were thought to be stable against photocorrosion[9]. Recently Gray Kline[10] et al. reported stable and efficient photoelectrochemical solar cells constructed with n-MoS_2 and n-WSe_2 as photoanodes in the form of single crystals. Polycrystalline

and thin films of molybdenum disulphide have been suggested as photoelectrode material in photoelectrochemical [Semiconductor-liquid junction cells][9-11]. Hence in the present investigation attempt has been made to prepare molybdenum sulphide thin films by spray pyrolysis technique and to understand certain electrical and optical properties of the films, keeping a view of their use in photoelectrochemical cells as photoelectrode.

1.2 Survey of Related Literature on Molybdenum Disulphide :

The most important sulphide formed by molybdenum is molybdenum disulphide (MoS_2) and it's occurrence as molybdenite. Molybdenum disulphide was prepared by Berzelius[12] by heating one of the higher sulphides in a closed vessel, and by heating molybdenum trioxide admixed with sulphur. Guichard[12] obtained the same compound by heating a mixture of 50 gms of ammonium m olybdate and 100 gms of sulphur and some lamp black. Berzelius[12] described molybdenum disulphide as a black powder while Pechard as a reddish-brown precipitate. Molybdenum disulphide crystals are hexagonal in form. In the hexagonal stacking polytype (denoted by 2H) the Mo atoms lie between planes of hexagonally packed S atoms forming as S-Mo-S snadwich layer in which the Mo atom is in trigonal prism co-ordination with the surrounding six S atoms, three in the upper plane and three in the lower one. For molybdenite Joly[12] reported temperature of sublimation and melting point to be 450°C and 1185°C respectively. Molybdenum disulphide

shows a photoelectric change in resistance when subjected to e.m.f. and exposed to thermal radiation. Doelter[12] found that the electrical conductivity of MoS_2 at ordinary temperature is small. The conductivity is increased as the temperature is increased.

MoS_2 is wellknown for its use as a solid lubricant for rotating and sliding components[13]. Thin sputter-deposited MoS_2 films have shown excellent lubricating properties[14]. The coefficient of friction can range from 0.04 which is effective lubrication to 0.4 which shows absence of lubricating property. The use of a semiconducting transition metal dichalcogenider like MoS_2, WSe_2 as the working electrode in photoelectrochemical (PEC) cell was pioneered by Tributsch[4-7]. Irradiation of these materials with visible light results in d-d band transitions[9] therefore these materials were thought to be stable against photocorrosion. MoS_2 has a high resistance to photocorrosion since light absorbed by this compound causes excitations of electrons from non banding molybdenum d orbitals. In particular MoS_2 have been studied with regard to stability and energy conversion efficiency. Molybdenum also forms molybdenum trisulphide (MoS_3), molybdenum tetrasulphide (MoS_4) and molybdenum pentasulphide (Mo_2S_5).

1.3 Theoretical Background

1.3.1 Electrical Transport in Semiconducting Films :

The study of electrical transport properties of solids is necessary to understand the use of solids in solid-state

devices such as photoconducting cells, solar cells. The basic transport properties are the electrical conductivity, the thermoelectric (Seebeck) coefficient Hall coefficient and magneto-resistance. From these properties one can get the information about the type, the mobility and the density of the majority charge carriers. The type and the density of the charge carriers do not much differ for a material in the bulk and thin film form.

1.3.2 Thermoelectric Power

The thermoelectric effect (Seebeck effect) is the generation of an open-circuit voltage when the temperature gradient is maintained across the thin semiconducting film (width $<$ length). The charge carriers at the hot end have higher thermal energy and large average velocity than those at the cold end. This uneven distribution of velocities results in a net flux of majority carriers towards the cold end. In the steady state the charged carriers produce an electric field which oppose any further net migration, hence for n-type semiconductor the hot end becomes positive and cold end becomes negative. The reverse is the situation for p-type semiconductor. The open circuit voltage thus produced across the semiconductor is called thermo e.m.f. and the effect is termed thermoelectric effect (Seebeck effect). The ratio of this thermally generated voltage to the temperature difference across the two terminals of the semiconductor is called thermoelectric power or thermoelectric coefficient. Thermoelectric power (α') measurements

help to calculate the carrier density and carrier mobility. This also gives information about the type of the material n- or p- .

Thermoelectric power is related to the majority carrier density in the material, and can be derived from the Boltzmann equation. The Boltzmann equation for a sample in the presence of electric field ϵ_x and temperature gradient d_T/d_x along the x axis can be written as

$$f = f_o + Te\, \epsilon_x V_x \frac{\partial f_o}{\partial E} - TV_x \frac{\partial f_o}{\partial x} \qquad \ldots (1.1)$$

where

f	=	perturbed fermi distribution function
f_o	=	equilibrium fermi-distribution function
V	=	thermal velocity
E	=	average energy of the carriers
T	=	relaxation time.

Since the equilibrium distribution function, f_o is known and $\partial f_o / \partial x$ can be written in terms of $\partial f_o / \partial E$, equation (1.1) becomes

$$f = f_o + TV_x \frac{\partial f_o}{\partial E} [e\epsilon_x + T\frac{d}{d_T} (\frac{E_F}{T}) \frac{d_T}{d_x} + \frac{E}{T} \frac{d_T}{d_x}] \quad \ldots \quad (1.2)$$

where E_F - energy difference between the bottom of conduction band and the fermi level. The current density in the x direction is given by

$$J_x = - e \int n(k) \; f \; V_x \; d_k \qquad \ldots \quad (1.3)$$

Where $n(k)\ d_k$ is the number of states per unit volume with k in the element d_k. For n type semiconductor, the current density can be written as

$$J_x = \frac{n_e}{m_e^*} [\ e\mathcal{E}_x + T \frac{d}{d_T} (\frac{E_F}{T})\ ](T) - \frac{n_e}{m_T^*} \cdot \frac{d_T}{d_x} (TE) \quad \dots (1.4)$$

where

$$T_E{}^i = \frac{\int_0^\infty (TE^i)\ E^{302}\ f_o\ d_E}{\int_0^\infty (TE^i)\ f_o\ d_E} \quad \dots \quad (1.5)$$

and m_e^* - is an effective mass of electron. If no current is allowed to flow, then $J_x = 0$ and electric field $\mathcal{E}_x$ obtained from equation (1.4) is given by

$$\mathcal{E}_x = T \frac{d}{d_T} [\ \frac{(TE) - E_F (T)}{eT\ (T)}\ ] \frac{d_T}{d_x} \quad \dots \quad (1.6)$$

The Thomson coefficient δ is related to the electric field $\mathcal{E}_x$ by the relation

$$\mathcal{E}_x = - \delta \frac{d_T}{d_x} \quad \dots \quad (1.7)$$

In case of semiconductor material with a temperature difference ΔT at the two ends where the metal contacts are made, the Thomson Coefficient of the semiconductor δ_S is given by

$$\delta_S = T \frac{d\alpha'}{d_T} \quad \dots \quad (1.8)$$

where α' is the thermoelectric power of the semiconductor. Comparison of equations (1.6), (1.7) and (1.8) leads to

$$\alpha' \equiv \frac{E_F(T) - (TE)}{eT\ (T)} \qquad \ldots \quad (1.9)$$

For a non-degenerate semiconductor and if T is of the form $T = aE^{-S}$, equation (1.5) and (1.9) gives

$$\alpha' = -\frac{k}{e}\left[\left(\frac{5}{2} - S\right) + \frac{E_F}{kT}\right]$$

$$= -\frac{k}{e}\left[A + \ln\frac{N_c}{n}\right] \qquad \ldots \quad (1.10)$$

where k = Boltzmann constant

$A = (\frac{5}{2} - S)$ = thermoelectric factor

N_c = density of states in the conduction band

n = electron density in the conduction band.

1.3.3 Dark Conductivity :

The excitation of an electron from the valence band to the conduction band creates an electron deficiency (hole) in the valence band. Both, electrons and holes, move in the conduction and valence bands respectively under the applied electric field resulting in conductivity in a semiconductor which is given by

$$\sigma = e\,(n\,\mu_n + p\,\mu_p) \qquad \ldots \quad (1.11)$$

and is called dark conductivity if measurement is made in dark. The conductivity of a semiconductor depends on the density of impurity levels, their distribution and, on the band gap energy (E_g). If the mobilities of the charge carrier do not vary,

conductivity is given by

$$\sigma = \sigma_0 \exp(-\Delta E / KT) \quad \ldots (1.12)$$

1.4 Absorption Processes in Semiconductors :

The absorption by bound and free electrons are both significant in semiconductors. There are altogether four types of electrons - (1) Inner shell electrons (2) Valence band electrons (3) Free carriers- including holes as well as electrons (4) Electrons bound to localized impurity centers. The first group do not contribute to absorption. Absorption by the second type of electron is of the greatest importance in the study of the fundamental properties of semiconductors.

In an ideal semiconductor at zero temperature the valence band would be completely full, so that an electron could not be excited to higher energy state within the band. The only possible absorption is that of quanta sufficiently energetic for the electrons to be excited across the forbidden zone into the empty conduction band. The resulting absorption spectrum is a continuum of intense absorption at short wavelength, bounded by steep absorption edge.

The transitions of electrons from valence band to conduction band can be grouped into direct and indirect optical transitions. In direct transitions the conduction band minimum and valence band maximum occur at $K = 0$ as shown in fig.1.1(a). In this case the absorption edge occurs at $h\nu = E_g$, where E_g

is minimum width of the forbidden zone or the activation energy of the semiconductor. Electrons with a given wave number in a particular band can only make transitions to states at higher band having the same wave number, i.e. in fig.1.1(a) only vertical transitions are allowed. For indirect transitions the wave vector K of electron changes in K-K space. Since phonon is emitted or absorbed in this case, resulting momentum will change. Fig.1.1(b) shows the indirect transitions.

The direct and indirect transitions can be differenciated by the dependence of α on the photon energy $h\nu$. For direct transitions the dependence of α on $h\nu$ is given by[22]

$$(n\alpha h\nu) \propto (h\nu - E_g)^{1/2} \quad \text{for allowed transitions}$$

and

$$(n\alpha h\nu) \propto (h\nu - E_g)^{3/2} \quad \text{for forbidden transitions,}$$

For indirect transitions the dependence of α on $h\nu$ is given by

$$(\alpha) \propto (h\nu - E_g)^2 \quad \text{For allowed direct transitions at } k = 0$$

and

$$(\alpha) \propto (h\nu - E_g)^3 \quad \text{For forbidden direct transitions at } k = 0 .$$

1.5 Purpose of Dissertation :

Thin films of molybdenum disulphide have created interest due to their use as photoelectrode material in photoelectro-

-chemical cells[9-11]. Although much work has been already done on structural, electrical and optical properties of molybdenum disulphide in the form of single crystals[14-20], very little data are available on the study of thin films of molybdenum sulphide. Therefore the present work is undertaken with a view to reveal some of the electrical and optical properties of molybdenum sulphide films prepared by spray pyrolysis technique.

(1) Deposition of the Films

The molybdenum sulphide films used in the study are prepared by spray pyrolysis technique, developed by Chamberlin and Skarman[20] and details worked out by Wu and Bube[21]. With this economical and reproducible process uniform and large area films are formed on glass substrate kept on hot plate, by spraying aqueous solutions of ammonium heptamolybdate and thiourea.

(2) Electrical Properties

From the view point of applicability of such films in solid state devices such as photoconducting cells, solar cells, their electrical properties are studied. The electrical properties such as dark conductivity, thermoelectric power help to determine the activation energy, carrier concentration, carriber mobility. The activation energy for conduction, carrier concentration, and carrier mobility characterise the properties of semiconductor. We have, therefore, studied dark conductivity-temperature behaviour and thermoelectric power.

(3) Optical Properties

In order to understand the band structure of the semiconductor and to determine the refractive index, extinction coefficient; the R_p / R_s reflectivity measurements method is used. The optical properties are studied as a function of the wavelength.

Figure Captions

1.1(a) Transitions between conduction and valence bands in direct band gap materials.

1.1(b) Transitions between conduction and valence bands in indirect band gap materials accompanied by emission of photons.

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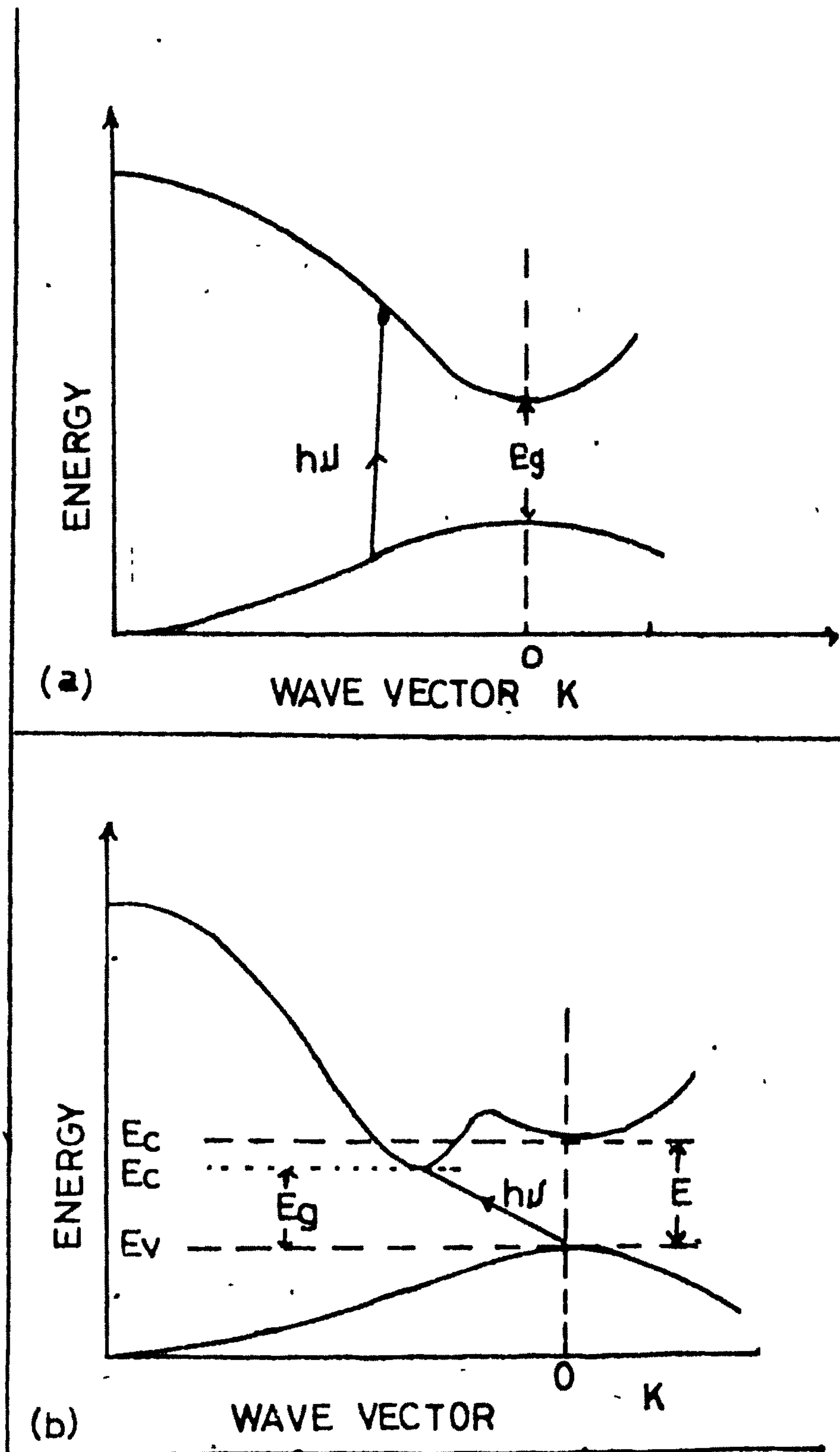

FIG. 1.1