Chapter 1

INTRODUCTION

The impact of thin film technology on the spectacular developments in the field of microelectronics during the last two decades had been tremendous. This was one of the most stimulating factors which helped the efforts to increase the understanding of thin films and to improve the level of sophistication of their deposition techniques. The recent discovery of the possibility of the production of p-n and p-i-n junctions using hydrogen passivated amorphous silicon thin films, coupled with mass producibility of large area non-epitaxial growth on any substrate material, match very timely with the strong current need for the development of a low cost solar cell as a new energy resource for terrestrial applications. Along with this, the increasing requirement of the optical industry and magnetic information storage devices also boosted the interest in the field of thin films.

A thin film is defined as a thin layer of a material whose one dimension is negligibly small compared to the other two dimensions and is created by the condensation process of atoms or molecules. Depending upon how the atoms or molecules are created from the bulk material for the condensation
process, the methods of depositing thin films are termed physical vapour deposition (PVD) or chemical vapour deposition (CVD) [1]. A brief review of this is given in Chapter 2.

If we go through the early history of thin films, it can be seen that during the ancient periods thin films were used for decorative purposes. Over three centuries back itself non-solid films were studied to explain the interference colours associated with thin oil layers on water surfaces. But the first solid films were obtained by Bunsen and Grove in 1852 by means of chemical reaction and by glow discharge sputtering respectively [2]. In the post war period, it was the boom in the use of silicon based microelectronic devices that gave a respectable position to thin film technology. In a sense we can say that the development of thin films was directly connected with the growth of semiconductor industry. Since the work presented in this thesis is centred around the preparation and characterization of amorphous silicon thin films, it is important to review the developments in this field over the last few decades.

Semiconductors are materials whose electrical resistivity at room temperature is in the range $10^{-2}$ to $10^9$ ohm cm (which is between that of a metal and an insulator) in which the electrical charge concentration increases with increase of temperature over some temperature range [3]. The
important semiconductors are elemental ones like silicon, germanium and selenium and compounds such as gallium arsenide, cuprous oxide, lead telluride and lead sulphide. Semiconductors are of three types according to their structure. They are crystalline, polycrystalline and noncrystalline. A crystalline semiconductor is characterized by the presence of long range periodicity. In other words, in a crystalline semiconductor, the surroundings of an atom will be exactly the same whatever be the position of the atom inside the crystal. This is because the atoms are arranged in an ordered lattice and the order extends throughout the crystal. A polycrystalline material is composed of many very small crystallites. In a noncrystalline material there is only short range order (SRO). That is, the immediate surroundings of an atom will be the same as that in a crystal. But as we go away from the reference atom, the very small deviations in the bond lengths and bond angles become appreciable and at a distance of the order of the tenth neighbour or so, the atoms are located essentially at random. Since noncrystalline semiconductors are predominantly covalently bonded, the lowest energy local configuration of each atom is almost always one in which its chemical valence requirements are fulfilled.

There are two main classes of noncrystalline semiconductors, the glasses and the amorphous films. Glasses are
those materials which can be quenched from the supercooled melt and usually exhibit a glass transition. The melts of most crystalline solids have viscosities less than 1 poise near the melting temperature \( T_m \). Some of these melts can be supercooled by nearly 10-20 degrees below \( T_m \) without crystallization. Their viscosity increases rapidly with decreasing temperature \([4]\). It reaches a value of \( 10^7 \) poise near \( T_m \). The viscosity continues to increase with decreasing temperature, and when it becomes \( 10^{14} \) poise the supercooled liquid becomes a solid glass. The process of glass transition which leads to the freezing of a supercooled liquid at \( T = T_g \) (glass transition temperature) into a noncrystalline solid (glass) is still an actively investigated theoretical problem \([5]\). Even though glasses were known for over thousands of years, the beginning of the systematic study of the noncrystalline materials started only in 1950's when Kolomiets showed that the chalcogenide glasses behave like intrinsic semiconductors and that their electrical conductivity could not be altered by adding dopants \([6]\).

Usually the term amorphous materials are restricted to those noncrystalline materials which can normally be prepared only in the form of thin films by deposition on substrates which are kept sufficiently cool to prevent crystallization. Amorphous films, in contrast to glasses, can exist in many different configurational states depending upon the
preparation techniques and upon a variety of substrate parameters. Annealing can lower the energy of a given amorphous film.

Although many defects common in crystalline solids like vacancies, interstitials, dislocations and grain boundaries are not likely to be found in the absence of periodicity, chemical defects such as undercoordinated or overcoordinated atoms and wrong bonds are quite possible. All glasses have intrinsic defects defined as the deviations from the lowest energy bonding arrangements [7,8]. Of all possible deviations from the ideal bonding configuration, the one that requires the least amount of energy will naturally be present at the highest concentration. The least energy requiring defects in chalcogenide glasses are the valence-alternation pairs (VAP). VAPs are two defects simultaneously created, one due to a positively charged overcoordinated atom and the other due to a negatively charged undercoordinated atom. They are known as VAPs because the valence or coordination is altered for the defect atoms. This never happens in a tetrahedrally bonded solid, since four is the maximum possible covalent coordination using 's' and 'p' orbitals. However large defect densities can exist in this material in the form of two fold and three fold coordinated atoms.
Experimental data on electrical transport properties can only be properly interpreted if a model for the electronic structure is available. For crystalline semiconductors, the main features of the energy distribution of the density of electronic states are the sharp structure in the valence and conduction bands and the abrupt terminations at the valence band maximum and the conduction band minimum. The sharp edges in the density of states produce a well defined forbidden energy gap. These specific features of the band structure are consequences of the long range and short range order. Since the short range order is present, the concept of the density of states is applicable to noncrystalline solids also.

In 1970 Mott argued that the spatial fluctuations in the potential caused by the configurational disorder in amorphous materials can create localized states in the form of a tail above and below the normal bands [10]. This argument was based on a theory by Anderson [11]. The states are called localized in the sense that an electron placed in a region will not diffuse at zero temperature to other regions with corresponding potential fluctuations.

Two most important band models for amorphous semiconductors are due to Cohen, Fritzsche and Ovshinsky (CFO model) and Davis and Mott [12,13]. The former describes a
simple band model based on the common features of the covalent amorphous alloys. It assumes that the tail states extend across the gap in a structureless distribution. This gradual decrease of the localized states destroys the sharpness of the conduction and valence band edges. The tails overlap at the centre. CFO model was specifically proposed for the multi-component chalcogenide glasses. Since in these materials, most atoms satisfy their valence requirements, there must be a valence band of extended states despite the randomly differing valencies and an energy band corresponding roughly to an energy for breaking valence bonds. However there will be mobility edges above and below the valence and conduction bands. At these mobility edges the mobility of the charge carriers change abruptly. The empty valence band tail states give rise to a random distribution of localized positive charges neutralized on the average by a corresponding distribution of an equal number of localized negative charges which are associated with the occupied conduction band tail states. These charged states above and below the Fermi level ($E_F$) act as efficient trapping centres for electrons and holes respectively. If we consider that the transition from the extended states to the localized states occur at energies $E_V$ for the valence band and $E_C$ for the conduction band, then we can expect a sharp drop in the mobility of the carriers at these energies as we pass from the extended states to the
localized states. The presence of the mobility edges explain why a well defined activation energy (ΔE) is observed for conductivity (σ) despite the lack of sharp band edges.

According to Davis and Mott model, the tails of localized states should be rather narrow and should extend a few tenths of an electron volt into the forbidden gap. Generated due to the defects in the random network, like dangling bonds and vacancies, a band of compensated levels exist near the mid gap according to this model. This band may be split into a donor and an acceptor band which will also pin the Fermi level. Mott suggested that at the transition from extended to localized states the mobility drops by several orders of magnitude producing a mobility edge. The energy interval between the two mobility edges acts as a pseudogap and is defined as the mobility gap.

The first proposal of a model showing bands of donors and acceptors in the upper and lower half of the mobility gap was introduced by Marshall and Owen in 1971 [14]. It is clear now that the density of states of an amorphous semiconductor does not decrease monotonically into the gap, but shows many peaks which can be well separated from each other. The position of the Fermi level is largely determined by the charge distribution in the gap states.
On the basis of Davis-Mott model there can be three processes leading to conduction in amorphous semiconductors. Their relative contribution depends upon the ambient temperature. At very low temperatures, conduction can occur by thermally assisted tunnelling between states at the Fermi level. At higher temperatures, charge carriers are excited into the localized states of the band tails. This conduction is by hopping. At still higher temperatures, carriers are excited across the mobility edge into the extended states. The mobility in the extended states is much higher than that in the localized states.

Now let us go a bit deep into the problem of amorphous silicon. Since the material has only one component, there is no question of compositional disorder. In amorphous silicon almost every atom is surrounded by four neighbouring atoms 2.35 Å away, exactly the same atomic separation as in the crystal. Even the second neighbours are essentially at the same distance as in the crystal, but there is a spread in the separations which reflect bond-angle deviations of about ±10° [4]. This spread becomes more and more significant as we go away from the reference atom and the order is lost roughly at the distance of the tenth neighbour. Thus in pure amorphous silicon, strictly speaking, there is a short range order only up to about 5 Å [5]. It is known that properties
of solids on an atomic scale whether crystalline or amorphous should be dominated by local chemical valence considerations as in the chemistry of molecules [13]. However, specifications of the short range order does not fully determine the structure of an amorphous semiconductor. One must also determine the distribution of ring sizes which can have important consequences on electronic states [14]. Ideal geometrical model of amorphous silicon historically is divided into two classes: microcrystalline and random network [15]. In the microcrystalline model, regions of crystalline-like order are connected by disordered boundaries, while in the random network model, there are no regions of crystalline order. For microcrystallites smaller than a few lattice constants in size, the structure is essentially a random network.

There are experimental evidences for the existence of large concentrations of spinless defects in amorphous silicon films. The observed spin density is almost always several orders of magnitude lower than the density of localized states in the gap [6]. When atomic hydrogen is introduced into pure silicon films, approximately hundred times as much hydrogen enters than the unpaired spin density suggests [7]. These unpaired silicon bonds are the most important defects in amorphous silicon films. They are also known as the dangling bonds. They occur with a density of $10^{18}$-$10^{20}$ per c.c. in nominally pure amorphous silicon. The higher
concentrations occur in sputtered, evaporated, or ion-bombarded layers that are prepared below 200-300°C. Higher temperature deposits, most notably chemical vapour depositions by the pyrolysis of silane near 600°C, have spin densities at the lower end of the observed range. This is because in this case the unpaired silicon bonds are passivated by hydrogen atoms. For the point of illustrating the microscopics of hydrogenation, it is enough to consider the idealized planar representation of a trivacancy as shown in Figure 1.10. When the material is hydrogenated not only the dangling bonds but the adjacent back bonds are also likely to pick-up H atoms, since they tend to be weaker than the typical Si-Si bonds within an ideal Si network. It is seen that many hydrogen atoms can be incorporated in the vicinity of a single paramagnetic defect. A paramagnetic site is composed of two aligned but unpaired bonds. In fact hydrogen can also be taken up by the nonparamagnetic multivacancies as well. It therefore explains why more hydrogen atoms are present in hydrogenated amorphous silicon than the number of paramagnetic centres in pure amorphous silicon [8]. Furthermore, due to the nature of the disorder itself there can be other weak bonds (Si-Si bonds with bond lengths other than the ideal 2.35Å) within the random network and these bonds may also be easily broken apart and then terminated by hydrogen atoms [9].
Fig. 1.10

Idealized planar representation of a tri-vacancy: upper) In pure Si. lower) In hydrogenated Si.
Early theoretical work suggested that the addition of hydrogen to the amorphous silicon matrix would remove states from the top of the valence band [16]. In the case of crystalline silicon it was observed that electronic energy levels of the dangling and weak bonds lie within the band gap. Hydrogenation of crystalline silicon surfaces removes gap states and replaces them with Si-H bonding levels deep down in the valence band and antibonding levels in or near the conduction band [8]. Thus the effect of hydrogenation of amorphous silicon is the removal of states from within the band gap [10]. Early theoretical work suggested that the addition of hydrogen to the amorphous silicon matrix would remove states from the top of the valence band [16]. This work suggested that the observed widening of the gap with increasing hydrogen content occurs primarily by depletion of states from the valence band edge [17-19]. The Si-H energy levels lie away from the band gap and hence do not interfere with the near band gap transport and optical phenomena which are of prime importance to the semiconductor physicists.

It was Sterling and his collaborators at the S.T.L. Laboratories who first prepared thin films of amorphous silicon and amorphous germanium by the decomposition of the hydride in an r.f. glow discharge in the mid sixties [28-30]. Towards the end of 1968 a group at the University of Dundee
in U.K. started working in amorphous semiconductors [31]. Their aim was to provide some reasonably conclusive experimental tests of the proposed models and transport mechanisms. In the early stages of their work they found that thin films of amorphous silicon and amorphous germanium produced by the glow discharge technique were the most promising ones in which the basic properties of the amorphous phase were not obscured by a high density of defect states. In 1970 they published the first electron drift mobility results on glow discharge a-Si [31]. The first experimental information on the density of states in the energy gap was published by Spear and LeComber in 1972 [32]. During 1973 and 1974 a fairly detailed study of the optical and photoconductive properties of glow discharge produced silicon was carried out at Dundee, in which it was attempted to correlate the photoconductive behaviour with transport results and the density of state distribution [33,34].

In 1975 LeComber and Spear showed that the electronic properties of a-Si and a-Ge prepared by the glow discharge method could be controlled by substitutional doping in a systematic way over a wide range [35,36]. This was a remarkable step forward in the development of a-Si and it was quickly followed by the fabrication of the first a-Si p-n junction [37]. Soon after this, development of a-Si photovoltaic
devices was reported from the RCA laboratories [38]. This caused an explosion in the number of research papers coming out on the preparation and characterization of a-Si:H thin films and solar cells. Most of the research groups concentrated on the glow discharge method of film production while a relatively few groups worked on sputtered and evaporated amorphous silicon in an atmosphere of hydrogen [39,40]. It was soon established that post hydrogenated amorphous silicon films have certain advantages over the conventional glow discharge produced ones. They are the absence of the so called Staebler-Wronski effect (which is a light induced instability), reduction in the amount of hydrogen going into the interstitial positions and the better control over the amount of hydrogen incorporated into the film [41-43]. However, this method is the least investigated one. This is probably due to the early success of the glow discharge method.

During the past decade considerable efforts have been expended in attempts to characterize and understand the electronic properties of amorphous silicon films. Electrical conductivity studies are very important among them. The d.c. electrical characteristic of a-Si and a-Si:H films are carried out by many groups of researchers [44-49]. Due to Si-H bond formation the electrical conductivity and the density of gap states decreases. Also, due to hydrogenation, the Fermi level
shifts towards the conduction band and the extended state conduction becomes dominant at room temperature [43].

Just like the d.c. conductivity, the frequency dependent conductivity (a.c. conductivity) is also an important parameter to characterize an amorphous material. Under favourable circumstances the a.c. conductivity studies can be used to make an estimation of the density of states of amorphous materials [50-52]. Many reports have appeared on the a.c. conductivity of different amorphous materials [53-56] but that of a-Si:H is extremely rare. Mott [52] has shown that all the three conduction mechanisms that contribute to the d.c. conduction can contribute to the a.c. conduction also. They are the conduction through the extended states, conduction by carriers excited into the localized states at the edges of the valence or conduction band and hopping transport by carriers with energies near the Fermi level.

The change in the d.c. conductivity of a-Si and a-Si:H thin films due to exposure to different gas ambients is a rarely investigated but nevertheless a very important study. It gives information on the conductivity type of the film. This study also gives an explanation to the inconsistencies in the reported values of various electrical parameters of a-Si:H films prepared in different laboratories. Tanielian et al. have carried out such an investigation on a-Si:H thin
films prepared by glow discharge [57] and have found that different gas ambients have profound effects on the electrical characteristics of these films.

Due to these reasons a systematic study was carried out on the d.c. and a.c. electrical properties of a-Si and a-Si:H films prepared by vacuum evaporation. It was observed that various preparation parameters like substrate temperature, annealing temperature, annealing time, film thickness, hydrogenation temperature and hydrogen partial pressure play very important roles in shaping the electrical characteristics of these films.

The first major application of amorphous semiconductors was in the field of Xerography. This process utilizes the photoconductivity of certain high resistivity amorphous semiconductors containing selenium. The photoconductive properties of chalcogenide glasses are used in an image pick up tube known as saticon developed by Hitachi and the Japan Broadcasting Corporation for use in small colour television cameras [58]. Memory switching has been observed in many amorphous semiconductors including a-Si:H [59]. This phenomenon is used by many companies for developing an electrically alterable, read-only computer memory. Hydrogenated amorphous silicon films are widely used in the fabrication
of photoconductivity cells. These cells are used as light sensing elements in certain types of light meters and light activated switches. It is found that rectifying junctions could be fabricated by sputtering amorphous silicon into crystalline silicon substrates [60]. In certain cases when such a a-Si:H diode is forward biased, it emits light due to electroluminescence [61] with a peak photon energy of \(~1.2-1.3\) eV. However, as discussed earlier, the most important application of a-Si:H has been in the low-cost solar cells [62]. Band gap of a-Si:H is ideal for solar energy conversion. Another very important application of amorphous silicon is in the fabrication of thin film field effect transistors. In 1976 itself there were proposals for the use of amorphous silicon field effect devices in the addressing of liquid crystal matrix displays as an alternative to thin film CdSe transistors. It was Neudeck and Malhotra [63] who have first fabricated thin film field effect transistors using evaporated amorphous silicon. They have made use of thermally grown SiO₂ as the gate insulator and photolithography techniques to define the shape of the aluminium source and drain electrodes. At present the main application of amorphous silicon FETs is in the liquid crystal display devices. The transient behaviour of an FET in the liquid crystal matrix is mainly determined by the capacitive loading of the liquid crystal element. It is possible, even with the present amorphous silicon
devices, to address about 1000 lines in 40 ms which is the charge retention time of the elementary liquid crystal capacitor in the off state of the FET. Recently it was shown that an integrated inverter circuit [64] and an image sensor [65] can be fabricated from amorphous silicon FETs. It is also reported that the fabrication of NAND and NOR gates is also possible with amorphous silicon FETs. The main limitation of the present devices is their low value of gain-bandwidth product. Attempts to improve this are carried out by many research groups.

In order to check whether the vacuum evaporated and post hydrogenated amorphous silicon films prepared in the present case can be used to fabricate electronic devices, elementary field effect transistors were fabricated in the coplanar structure and is discussed in detail in this thesis. The experiment was reasonably successful and indicated that optimization of preparation parameters and film thickness would yield better devices.

If a-Si:H is a new comer in the field of electronic materials, cadmium sulphide is one of the oldest and extensively investigated semiconducting materials. Relatively early in the research of photovoltaic effect and the development of solar cells, II-VI compounds have played an important role. Almost at the same time as the silicon solar cells were first
described [66], the photovoltaic effect in CdS/Cu$_2$S was reported [67]. A variety of II-VI based solar cells are known and actively investigated. It can be seen that the most prominently researched II-VI based solar cells are CdS/Cu$_2$S cells, CdS/CuInSe$_2$ cells or those with Cd$_x$Zn$_{1-x}$S. A large number of techniques are employed for the deposition of CdS films, prominent among them are evaporation, spray pyrolysis and screen printing. Each of these methods has its own advantages and disadvantages [68-70]. Technologists are therefore on the lookout for newer methods in order to tailor the properties of the films to suit their needs. Of the several methods available, chemical methods have certain advantages for the fabrication of CdS thin films, since they are cheaper and easier compared with the physical methods. These very reasons will give chemical methods an upper hand in the future, at least as far as solar cells are concerned, if large scale manufacturing of thin film solar cells is to be a reality for terrestrial applications. Eventhough the structure, d.c. conduction, photoconduction and photovoltaic effects of this material are well studied [68,70-73], its a.c. conduction mechanisms and dielectric properties are not so extensively investigated. Even, parameters which are well studied should be subjected to reinvestigation when the film is produced by a new method or by a modified form of one of the well known methods. Elliott's theory [51] is ideal for interpreting
the results of the a.c. conduction experiments in CdS, since the theory is originally developed for II-VI compounds. It can be used to calculate the density of states of CdS at the Fermi level which is a very important parameter for any semiconductor.

In this thesis the d.c. and a.c. electrical characteristics and dielectric properties of CdS thin films prepared by chemical bath deposition technique are presented. By slightly modifying the preparation method it was found possible to decrease the sulphur deficiency and as a result nearly intrinsic films were obtained.

The investigation presented in this thesis therefore covers detailed studies on the dielectric properties and a.c./d.c. conduction of a-Si and a-Si:H thin films prepared by vacuum evaporation. The influence of the various gas ambients has also been investigated in detail. Using these films a field effect transistor is fabricated and characterized. In the case of CdS, by modifying slightly the chemical bath deposition method, very nearly intrinsic films were obtained and characterized. These investigations in general results in obtaining important informations.
REFERENCES


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