Chapter 1

Amorphous Semiconductors and Amorphous Oxide Thin Film Transistors

First part of this chapter gives a broad introduction to amorphous semiconductors and their optical and electrical properties. Second part gives a review of thin film transistors limited to amorphous oxide channel devices.

1.1 Amorphous materials: An introduction

History of civilization is intimately connected with advances in material research. Materials science is an interdisciplinary area which comprehends the areas of physics and chemistry. Materials, in a broad sense, can be classified into crystalline and amorphous materials. A perfect crystalline material has a translational symmetry and a unit cell when extended in three dimensions give the structure of the material. Unlike the case of
crystalline materials, amorphous materials lack the long range periodicity. Until the end of last century, it was only the crystalline materials which got the attention of scientific community. It was believed that, due to the disordered nature of the amorphous materials, they will not find any technological applications.

In thermodynamic view point, an amorphous solid is in a non-equilibrium state; therefore its structure and bond configurations are not fixed but can be changed, sometimes reversibly, not only by thermal treatment but also by light irradiation. This is fundamentally different from the case of crystalline solids. Since amorphous phase is less thermodynamically stable (it possesses a greater free energy) than the corresponding crystalline form, the preparation of amorphous materials can be regarded as the addition of excess free energy to some manner into the crystalline polymorph. How this is done can vary widely, but it is a rule of thumb that the faster the rate of deposition or cooling, the further the amorphous solid lies from equilibrium.

The term “glass” and “amorphous” were widely used in the same sense in literature to describe the disordered materials. In a more precise form, usually the term “glass” is used for only those materials which can be quenched from the super-cooled melt and usually exhibit a glass transition and the term “amorphous” refers non-crystalline materials which can normally be prepared only in the form of thin films by deposition on substrates which are kept sufficiently cool to prevent crystallisation [1]. This convention will be followed when referring to “amorphous” materials throughout this thesis.

Randomness can occur in several forms, like topological, spin, substitutional, vibrational disorders etc (Figure 1.1) [2]. Disorder is not a unique
Figure 1.1: Types of disorder: (a) topological disorder (no long range order); (b) spin disorder on regular lattice; (c) substitutitional disorder on regular lattice; (d) vibrational disorder about equilibrium positions of a regular lattice.

property, and must be compared to some standards, and that standard is the perfect crystal. A perfect crystal is that in which the atoms are arranged in a pattern that repeats periodically in three dimensions to an infinite extend.

1.2 Structure of amorphous materials

Knowledge of the structural arrangement of atoms of a crystalline or amorphous solid substance is an essential prerequisite to any detailed analysis of the physical or chemical properties of the solids. Crystalline solids are characterised by long range periodic order. The constraint of three-dimensional periodicity imposes the severe limitation of the existence of only seven crystal systems, 32 crystallographic point groups, and 230 space groups
resulting from the application of the translational symmetry operations of the crystal. Once the lattice vectors $a_1, a_2, a_3$ and the position of the atoms within the unit cell are known, the positions of all the atoms in the crystal can be described simply because of the periodicity in three dimensions.

The determination of structure of amorphous solids is an exceptionally difficult task, and no single experimental technique is wholly sufficient. Instead of the exact structural properties, a type of statistical description of the atomic arrangement is sought. We look the average coordination of the each atomic species in the material, the types, numbers and the average distance to the near neighbours etc.

The different methods for structure determination include *Radial Distribution Function (RDF)*, *Extended X-ray Absorption Fine Structure (EXAFS)*, *diffuse scattering of x-rays and neutrons*, etc.

RDFs give the distances and coordination numbers out to third or forth neighbours and are useful for elemental amorphous materials. They are also extremely good for many oxide glasses and other systems where there are distinct distances that can be recognised, and where the structures of the amorphous materials are close to those of the crystalline. Under these circumstances, good models can be generated which fits the RDF. In many other polyatomic systems, the technique is far from good. In such cases, the A-A, A-B, and B-B neighbour distances are about the same, and all lead to one big broad first neighbour peak. As a result of that, one cannot obtain unique coordination numbers and unique structural interpretations of the RDFs.

EXAFS is atom specific since the x-ray absorption edge energy is characteristics of a given element and so the local structure around a particular type of element. In EXAFS, the scattering expression is a local function
and does not depend on translational periodicity; the technique is therefore equally applicable to crystalline and disordered materials. Structural information can be extracted by fitting the experimental amplitude to theoretical equations. EXAFS analysis yields information about the average atomic arrangement around a particular atomic species in the material. The drawback is that EXAFS provides information only about near neighbours in amorphous materials. EXAFS may even be misleading for near neighbours when there is a broad distribution of those neighbours.

1.3 Electronic states

The Hamiltonian describing a perfect crystal can be written as

\[
H = \sum_i \frac{p_i^2}{2m_i} + \sum_j \frac{p_j^2}{2M_j} + \frac{1}{2} \sum_{j', j} \frac{Z_j Z_{j'} e^2}{4\pi \varepsilon_0 |R_j - R_{j'}|} - \sum_{j, i} \frac{Z_j e^2}{4\pi \varepsilon_0 |r_i - R_j|} + \frac{1}{2} \sum_{i, i'} \frac{e^2}{4\pi \varepsilon_0 |r_i - r_{i'}|}
\]

where \( r_i \) denotes the position of the \( i^{th} \) electron, \( R_j \) is the position of the \( j^{th} \) nucleus, \( Z_j \) is the atomic number of the nucleus, \( P_i \) and \( P_j \) are the momentum operators of the electrons and nuclei respectively. Prime over summation means that, summation is only over pairs of indices which are not identical. Such a many particle Hamiltonian is solved by large number of simplifications. The approximation is to separate electrons into two groups: valence electrons and core electrons (electrons in filled orbitals). Since core electrons are mostly localized around the nuclei, they can be lumped together with the nuclei to form the ion cores. So the indices \( j \) and \( j' \) in the above equation denotes the ion core while the electron indices...
and \( i' \) label the valence electrons. The next approximation is the Born-Oppenheimer or adiabatic approximation. The ions are much heavier than electrons, so they move much more slowly. The electrons can respond to ionic motion almost instantaneously. Or, in other words, to the electrons the ions are essentially stationary. On the other hand, ions cannot follow the motion of the electrons and they see only a time averaged adiabatic electronic potential. Mean field approximation assumes that every electron experiences the same average potential \( V(r) \).

In almost all cases of crystalline solids, the one-electron approximation is applied to the Schrödinger equation, in which it is assumed that each electron moves in the average field due to all the others. This approximation neglects electronic correlations, i.e., the possibility that two electrons can correlate their motion in such a manner as to keep away from each other, and thereby minimise their repulsive interaction.

This formulation of solid state theory depends on the validity of both the adiabatic and one-electron approximations. In a wide class of materials, the effect of phonon coupling and electronic correlations are negligible, and theory and experiments are in good agreement. However, in some situation the electron-phonon interaction is large, and the adiabatic approximation becomes inaccurate. Similarly the one-electron approximation becomes erroneous in many cases. Electron-phonon interaction can be very strong in ionic solids. In order to correctly describe the transport in such materials, we have to consider the effects of polaron, small polarons etc.

The key element in the conventional approach to understanding the electronic structure of crystalline solids is the simplification of the problem by making use of the fact that the one-electron potential energy must exhibit the periodicity of the lattice. Theory can be applied to reduce the
problem to one involving the small number of electrons containing in a single primitive cell, from which the crystal can be generated. All electronic states are extended throughout the solid and have the same probability for finding in each of the primitive cells. The one electron density of states can be calculated by solving the one-electron problem in a single primitive cell and applying periodic boundary conditions. Because of the periodicity, the density of states (DOS) of any crystalline solid takes the form of alternating regions of energy with large densities, called bands separated from regions where no states are possible, called gaps.

Although conventional solid state theory has succeeded in explaining the behaviour of crystalline solids, it can be criticised on two major grounds [3].

1. This model completely neglects the short range order which reflects the chemistry of constituent atoms. For example, the symmetry of the primitive cells of covalently bonded c-Si is the exactly the same as that of metallic Ni and ionic NaCl, despite the very different local coordination.

2. The periodicity seems to be vital to the electronic behaviour of materials, which is inconsistent with experimental results. If periodicity were essential to the observed electronic transport in crystalline solids, we should expect large changes in conductivity upon melting, at which point the long range order spontaneously disappears. However, melting has only a very small effect on the conductivity of a large class of materials, including insulators, semiconductors, and metals. Thus, the basic DOS and mobility cannot be very sensitive to crystalline periodicity.
1.4 Effective mass concept

A charge carrier in any solid can only be made free by associating it with an effective mass through the effective mass approximation. As in the case of crystalline solids, theories have been developed by several authors for determining the effective mass of charge carriers in amorphous solids. As the wave vector $\mathbf{k}$ is not a good quantum number in amorphous solids, the derivation of effective mass of charge carriers has been done in real coordinate space. It enables to determine effective masses in the extended and tail states separately. The effective mass of a charge is inversely proportional to the width of the corresponding energy states at a fixed concentration of atoms contributing to the tail states [4].

1.5 Band models

A model for electronic structure of the material is essential for the proper interpretation of experimental data of electrical transport properties. Making use of mathematical simplifications resulting from the periodicity, Bloch was able to derive some general properties of the electronic states in the crystal, from which Wilson developed the band theory of electronic transport. Since their pioneering work, it is known that the electronic structure of the crystal shows some universal characteristics. For semiconductors, the main features of the energy distribution of the density of electronic states $N(E)$ of crystalline solids are the sharp structure in the valence and conduction bands, and the abrupt terminations of $N(E)$ at the valence band maximum and the conduction band minimum (Figure 1.9). The sharp edges in the density of states produce a well-defined forbidden energy gap.
Within the band the states are extended, which means that the wave functions occupy the entire volume. The specific features of the band structure are consequences of the perfect short-range and long-range order of the crystal. In an amorphous solid, the long-range order is destroyed, whereas the short-range order, i.e., the interatomic distance and the bond angle, is only slightly changed. The concept of the density of states is equally applicable to non-crystalline solids. The DOS in the energy space can be written as [5]:

\[
N(E) = \frac{V}{2\pi^2} \left( \frac{2m_e^*}{\hbar^2} \right)^{3/2} E^{1/2}
\]  

(1.2)

where, \( V \) is the volume of the sample, \( m_e^* \) is the electron effective mass and \( E \) the energy. This can be applied to both valence and conduction extended states using the respective effective masses of charge carriers. This form of DOS is not depend on the translational symmetry. The above form is obtained from the Schrödinger equation for a free electron by the boundary condition that, the Eigen functions must vanish at the sample boundaries and the normalisation condition that the electron is confined in a finite size sample. Above equation can, therefore, be applied to any solid, crystalline or non-crystalline, as long as it is a free electron system, because the above derivations are true only for free electron gas. If the electrons are not free, they can be made so by using the effective mass approach and then they will be free with that effective mass. Systems with different effective masses of their charge carriers will have different density of electron states. The DOS in amorphous solids is expected to be different since amorphous semiconductors have a different effective mass than compared to crystalline solids. For most of amorphous semiconductors, for energies, \( E > E_C \), in the con-
Figure 1.2: Schematic representation of DOS in crystalline semiconductors. Symbols: $E_V$ is valence band maximum energy, $E_C$ is conduction band minimum energy and $E_F$ is the Fermi energy.

duction states, and $E < E_V$ in the valence states, the dependence of DOS in the equation 1.2 on the energy agrees with observed values. Replacing $E$ by $(E - E_C)$ for conduction extended states and with $(E_V - E)$ for valence extended states in equation 1.2 suggest a sharp drop in the DOS at the mobility edges, which is against the observations in amorphous solids. This is because the derivation of DOS have only considered a fully coordinated network of atoms, which is usually not the case in any amorphous solid. There are also disorders present, which influence the DOS near the mobility edges.

Several models were proposed for the band structure of amorphous semiconductors, which were the same to the extent that they all used the concept of localized states in the band tails [6].
Figure 1.3: Schematic representation of DOS in CFO model. Symbols: $E_V$ is valence band energy edge corresponding to crystalline case, $E_C$ is conduction band energy edge corresponding to crystalline case and $E_F$ is the Fermi energy.

1.5.1 The Cohen-Fritzsche-Ovshinsky (CFO) model

The CFO model was specifically proposed for the multicomponent chalcogenide glasses [7]. The authors suggested that in the chalcogenide alloys, the disorder is sufficiently great such that the tails of the conduction and valence bands overlap, leading to an appreciable density of states in the middle of the gap (Figure 1.3). A consequence of the band overlapping is that there are states in the valence band, ordinarily filled, that have higher energies than states in the conduction band that are ordinarily unfilled. As a result, a redistribution of the electrons must take place, forming filled states in the conduction band tail, which are negatively charged, and empty states in the valence band, which are positively charged. This model, therefore, ensures self-compensation, and pins the Fermi level close to the middle of the gap.

One of the major objections against the CFO model was the high transparency of the amorphous chalcogenides below a well-defined absorption
edge. It is now almost certain from different observations that the extent of tailing in chalcogenides is rather limited.

1.5.2 The Davis-Mott model

Based on Anderson's theory, Mott showed that spatial fluctuations in the potential caused by the configurational disorder in amorphous materials may lead to the formation of localized states, which do not occupy all the different energies in the band, but form a tail above and below the normal band \[8\]. According to Davis and Mott, the tails of localized states should be rather narrow and should extend a few tenths of an electron volt into the forbidden gap. Further, defects in the structure, such as dangling bonds, vacancies, etc leads to a distribution of electron states in the middle of the gap, near the Fermi energy \(E_F\).

Figure 1.4 gives the Davis-Mott model; where, \(E_C\) and \(E_V\) represent the energies which separate the ranges where the states are localized and extended. The centre band may be split into a donor and an acceptor band, which will also pin the Fermi level (Figure 1.5). Mott suggested that at the transition from extended to localized states, the mobility drops by several orders of magnitude producing a mobility edge. The interval between the energies \(E_C\) and \(E_V\) acts as a pseudogap and is defined as the mobility gap \[9\]. Cohen proposed a slightly different picture for the energy dependence of the mobility \[10\]. He suggested that there should not be an abrupt but rather a continuous drop of the mobility occurring in the extended states just inside the mobility edge. In this intermediate range the mean free path of the carriers becomes of the order of the interatomic spacing, so that the ordinary transport theory based on the Boltzmann equation
Figure 1.4: Schematic representation of DOS in Davis-Mott model. Symbols: $E_V$ is valence band energy edge corresponding to crystalline case, $E_C$ is conduction band energy edge corresponding to crystalline case, $E_B$ and $E_A$ are valence band and conduction band tailing edge and $E_F$ is the Fermi energy.

cannot be used. Cohen described the transport as a Brownian motion in which the carriers are scattered continuously [10].

On the basis of the Davis-Mott model, there can be three processes leading to conduction in amorphous semiconductors. Their relative contribution to the total conductivity will predominate in different temperature regions (conduction mechanism in amorphous solids are discussed in section 1.7). 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; carriers in these localized states can take part in the electric charge transport only 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 in the localized states. Hence it follows that electrical conductivity measurements over a wide temperature range are needed to study the electronic structure of amorphous semiconductors.
1.5.3 Small-Polaron model

It is a rival theory for electrical conduction in amorphous solids, particularly for the case of chalcogenides. The term polaron refers to the quasi-particle unit comprising the self trapped carrier and the associated atomic displacement pattern (Figure 1.6). If the spatial extend of carrier’s wave function is severely localized on the scale of interatomic distances, the polaron is referred to as being small. If the wave function is of much large extend, it is said to be a large polaron. An important aspect of polaron formation in solids is that the size of the polaron that can be formed depends upon the range of the electron-lattice interaction. Small polaron band width is orders of magnitude smaller than that for non polaronic carriers. As a result, even rather modest disorder will produce Anderson localization in a system in which the carriers form the small polarons. Even in the absence of disorder, the energy uncertainty associated with the scattering of a small
Figure 1.6: The atomic displacement pattern about a self trapped electron is illustrated for the charge occupying each of two adjacent sites.

polaron can be larger than the small polaron bandwidth. In such instances, which are equivalent to the mean free path being smaller than the intersite separation, the transport is best characterised by being phonon assisted hopping motion with rather low mobilities which increases with increasing temperature. Disorder may produce sufficient localization to enable self trapping and concomitant extreme localization to occur [11].

Experimental evidence, mainly coming from luminescence, photoconductivity and drift mobility measurements, has been found for the existence of various localized gap states, which are split off from the tail states and are located at well-defined energies in the gap [12]. These states are associated with defect centers, the nature of which is not always known. It is clear now that the density of states of a "real" amorphous semiconductor does not decrease monotonically into the gap but shows many peaks which can be well separated from each other (Figure 1.7). The position of the Fermi level is largely determined by the charge distribution in the gap states. There is no systematic theory developed for amorphous semiconductors to demonstrate that the DOS within the gap is like what is shown in the figure 1.7.
1.5.4 Weaire and Thorpe model

The first demonstration, that short range order alone can produce an energy gap in the density of states (DOS) of a semiconductor, was given by Weaire and Thorpe [13, 14]. For tetrahedrally coordinated amorphous structures, they considered a Hamiltonian of the form;

\[
H = \sum_{i,j \neq j'} V_1|\phi_{ij}\rangle\langle \phi_{ij'}| + \sum_{i \neq i',j} V_2|\phi_{ij}\rangle\langle \phi_{i'j'}|
\]  

(1.3)

where the atoms are denoted by the subscript \(i\) and the bonds by \(j\), the states are localized sp\(^3\) hybrid orbitals, and the matrix elements \(V_1\) and \(V_2\) represent the intra-atomic and interatomic interactions, respectively (Figure 1.8). This Hamiltonian makes it easy to separate the effects of quantitative disorder (i.e., bond angle variations), reflected in a spread of values of \(V_1\) and \(V_2\), from topological disorder (i.e., variations in ring size). They showed that the bonds are essentially of bonding and anti-bonding charac-
Figure 1.8: Wcaire-Thorpe model showing intrasite ($V_1$) and intersite ($V_2$) interactions.

er, split by the $V_2$ term and broadened by the $V_1$ term, and the broadening of bonds by $V_1$ term does not destroy the gap created by the $V_2$ term. There is always a band gap between two allowed bands, except for the one value $V_1/V_2 = 1/2$, at which they touch.

The importance of the work was that the electronic structure of a system with a Hamiltonian given by equation 1.3 is independent of the structure in which the atoms are distributed, provided only that the local coordination of four neighbours (of tetrahedral coordination) is maintained throughout the structure. The inclusion of the effects of the local deviations from perfect tetrahedral coordination, together with the interaction of more distant orbitals, generally results in a finite (though presumably small) density of states in the band gap. With a more generalised Hamiltonian, they were able to show the existence of band gap in amorphous compound semicon-
ductors [15].

Thus, the existence of a band gap for a non-crystalline solid can be understood in terms of chemical concepts.

Other methods in the calculation of DOS of amorphous materials include:

1. Empirical tight binding technique: in which the matrix elements and overlap integrals are treated as adjustable parameters to be fitted to known experimental results.

2. Orthogonalised linear combination of atomic orbitals (OLCAO): makes use of expansions of atomic orbitals in terms of Gaussians, with the potential constructed from all the atoms in a small cluster.

3. Pseudopotential techniques: in which the real potential is replaced by much smoother effective potential that yields high accuracy results for the outer electronic states but not the core. This give more accurate results than tight binding methods.


5. Self Consisted Field $X_\alpha$ Scattered Wave (SCF-$X_\alpha$-SW) approach, and

6. Unrestricted Hartree-Fock (UHF) approach.

1.6 Optical absorption in amorphous semiconductors

The fluctuations in the atomic configurations away from the average are accompanied by the fluctuations acting on the electron. When the potential fluctuations are sufficiently deep or wide, the energies of the electronic
states are perturbed and results band broadening and band tailing [6]. The
symmetry properties of the electrons and of fluctuations of the local order
are both important in determining magnitude of the effect on the DOS.
For example, the energies of the s states are less sensitive to fluctuations
of the local coordination that have nearest neighbour distances fixed but
vary the orientation of the nearest neighbour atoms than are the energies
of p or d states. Thus the effect of disorder is expected to be different
for the valence and conduction band edges of amorphous semiconductors.
On the other hand, the probability of optical transitions between filled and
empty tail states is limited in large extend by the disorder induced or An­
derson localization of the electron states near the band edges. Transitions
are therefore allowed only to the extend that there is spatial overlap of
the localized wavefunctions. In contrast, transitions between localized and
delocalized states beyond the mobility edges are strongly allowed.

The destruction of $\vec{k}$ as a good quantum number in amorphous solids
affects the optical properties, independent of the extend of band tails. In
crystals, because of very small photon momentum, $\vec{k}$ is conserved in all
optical transitions which causes relatively weak optical absorption even
above the energy gap in indirect band gap crystalline materials. Since $\vec{k}$
is not a good quantum number in the absence of periodicity, this selection
rule is inappropriate for the amorphous solids. In polycrystalline solids,
each grain retains its periodicity, and $\vec{k}$ conservation remains applicable
even with a 50 Å grain size. The relative spread in $\vec{k}$, as estimated from
the uncertainty principle, is of the order of [1]

$$\frac{\Delta k}{k_{BZ}} \sim \frac{a}{L}$$

(1.4)
Figure 1.9: Schematic density of state diagram for a crystalline and an amorphous semiconductor in the vicinity of highest occupied and lowest empty states.

where $k_{BZ}$ is the maximum crystal momentum in the first Brillouin zone, $a$ is the size of the primitive cell, and $L$ is the grain size. For a 50 Å grain size, the spread in $k$ is less than 10% and is relatively insignificant. However, for smaller grain sizes there is a large spread in $k$ and presence of such deviations provide a more rigorous definition of an amorphous solid than does the range of the order. This is also a better criterion than one involving the existence of extensive band tails, since band tails can also arise from interface states at the grain boundaries of a polycrystalline solid.

The sharp features (discontinuities in the slope) in the DOS are the characteristics of crystalline solid (Figure 1.9). For a crystal, DOS function $N(E)$ is directly derived from the band structure $E(\mathbf{k})$ by simply counting
the states in $\vec{k}$ space. The sharp structures in $N(E)$ arises from the presence of special places in $\vec{k}$ space at which the gradient $\Delta_k E(\vec{k})$ vanishes. This occurs whenever $E(\vec{k})$ has a local maximum or minimum. Since $\vec{k}$ itself, as a quantum number labeling each electron eigenstate, depends for its validity upon translational periodicity, it follows that the sharp structure in $N(E)$ is a crystal property which requires long range order for its existence. In the absence of long-range order, these sharp features disappear.

As mentioned in the previous paragraph, the sharp structure in the electronic density of states $N(E)$ arises in a crystal as a band structure consequence of critical points in $\vec{k}$ space at which the gradient $\Delta_k E(\vec{k})$ vanishes. Since the first order allowed electronic transitions which dominate the ultraviolet region of the optical absorption spectrum of a crystalline semiconductor are $\vec{k}$ conserving direct transitions, that spectrum mirrors the joint density of states ($N_{cv}(E)$). Since $N_{cv}(E)$ is determined by $E_{cv}(\vec{k}) \equiv E_c(\vec{k}) - E_v(\vec{k})$ and thus has structure at energies corresponding to $\vec{k}$ values for which $\Delta_k E_{cv} = 0$, the crystal band structure similarly gives rise to structure in the optical absorption spectrum. These critical point spectral singularities (van Hove singularities), which are especially sharp in the crystal spectrum at low temperatures, are specific consequences of translational periodicity ($\vec{k}$ as a good quantum number). Hence, similar fine structure is absent in the amorphous spectrum.

In solids, the interactions between bonds broaden the bonding and antibonding levels into bands. The overall aspect of DOS is similar for both the crystalline and amorphous solid, since the overall electronic structure arises from the short-range order. $E_{av}$ (the energy difference between the centres of CB and VB) reflects the bonding-antibonding splitting. The effect of long range disorder in amorphous form (such as tailing of a finite DOS into
the pseudogap region spanned by $E_g$) do not wash out the main features of the optical transitions. Amorphous solids, lacking any special directions associated with crystallographic axes, are optically isotropic.

In tetrahedral semiconductors (Si, Ge etc) the conduction band (CB) originates from the antibonding levels and valence band (VB) from the bonding levels. In chalcogenide semiconductors, while the CB originates from the antibonding levels the highest VB is not formed from bonding states but instead from nonbonding or lone pair state. This causes chalcogenides their characteristics double peak feature of their UV spectra.

In a crystal, a photon of energy $h\nu$ can induce a transition from a filled state of energy $E$ to an empty state of energy $E + h\nu$ only if the initial and final states have the same wave vector ($\vec{k}$) and satisfy certain selection rules. Thus, among all the pairs of electron states separated by energy $h\nu$, only a very few contribute to optical absorption. But in a amorphous material, no such restrictions apply. Assuming that we are dealing with extended states, all such pairs of state (filled, at energy $E$, and empty, at energy $E + h\nu$) can contribute to optical processes.

1.6.1 Principle regions of optical absorption

Generally three distinct regions, A, B and C, are observed in the absorption coefficient of amorphous semiconductors near the electron mobility edge (schematically shown in figure 1.10). Above the mobility edge, in the region of strong absorption (region A in figure 1.10), the dependence of the absorption coefficient $\alpha$ on photon energy $h\nu$ can be described as $[16, 17]$,

$$\alpha h\nu \propto (h\nu - E_0)^2$$ (1.5)
where $E_0$ is the optical gap. Usually equation 1.5 is written as

$$(\alpha h\nu)^{1/2} = C(h\nu - E_0)$$

where $C$ is independent of the photon energy. A plot of $(\alpha h\nu)^{1/2}$ as a function of the photon energy $h\nu$ is called the Tauc plot, and the extrapolation of straight line region into the energy axis would give the optical gap $E_0$ (Tauc gap) [18–20]. Equation 1.6 is derived only for transitions from valence extended to conduction extended states, (without the involvement of any tail states) with the assumption that the matrix element is independent of the energies in the conduction and valence extended states. The optical gap thus obtained should correspond to the situation where there are no tail states, like in crystalline solids.
In the low absorption region (B region in figure 1.10), $\alpha$ increases exponentially with energy. In this region it can be written as

$$\alpha \propto \exp(h\nu/E_u)$$  \hspace{1cm} (1.7)

where $E_u$ is the width of the localized tail states and usually referred to as the Urbach tail. In the region C of figure 1.10, the absorption coefficient is written as another exponential function of the photon frequency

$$\alpha \propto \exp(h\nu/E_d)$$  \hspace{1cm} (1.8)

where $E_d$ is the width of the defect states, and usually it is found that $E_d$ is larger than $E_u$. The region C is rather sensitive to the structural properties of materials [21].
While there seems to be a general consensus about the Tauc plot of the absorption coefficient from valence extended states to conduction extended states, there are some experimental data which fit much better to the following relation

\[(\alpha h\nu)^{1/3} = C_F(h\nu - E_0)\]  \hspace{1cm} (1.9)

and have therefore used it to determine the optical gap \(E_0\). Here \(C_F\) is another constant [22]. The cubic dependence on photon energy can be obtained only when the DOS depends linearly on energy (instead of square root dependence as shown before), provided the assumption of constant transition matrix is valid for every amorphous solid.

In Cody’s method of evaluating the matrix element [23], it is considered as a dependent function of energy, which leads to an expression like:

\[(\alpha h\nu) = (h\nu)^2[h\nu - E_0]^2\]  \hspace{1cm} (1.10)

Thus there are two different ways of evaluating the transition matrix element. Applying one approach it is found to be independent of the energy and momentum of the excited charge carriers, but the second approach shows that it depends on the photon energy and hence on energy of charge carriers. If one uses the first approach, then \((\alpha h\nu)^{1/2}\) is found to give the correct Tauc’s plot (i.e. it is linear with the photon energy). However, if the second method was used, then \((\alpha/h\nu)^{1/2}\) would give the correct Tauc’s plot. As the objective of Tauc’s plot is to determine the optical gap, one may expect both approaches will produce the same value for the optical gap.
The DOS can be made to have parabolic dependence on energy (equation 1.2) for any particle by associating it with an appropriate effective mass. Then, the resulting absorption coefficient, obtained within the assumption of constant transition matrix element, will have the square root dependence on energy involving a different effective mass. In this view, a deviation from Tauc’s plot cannot be explained by assuming the constant matrix element. However, using energy dependent matrix element, the RHS of equation 1.10 is a forth-order polynomial. Depending on which term on the polynomial may dominate, one can obtain a deviation from Tauc’s plot. Therefore in a material in which a deviation from Tauc’s plot is observed, the transition matrix element may not be constant.

In chalcogenides the situation is more complicated since the DOS in the valence and conduction states are expected to have different form. This can also lead to a deviation from Tauc’s plot [4].

1.6.2 Transition in tail states

An exponential tail in the absorption coefficient of amorphous solids is usually observed for photon energies below the optical gap which is usually referred to as exponential tail or Urbach tail.

According to Abe and Toyozawa, the exponential densities of states in the tail region are caused by static disorder in amorphous solids [24]. The results also suggest that the effect of disorder plays role in the low energy region of the absorption, where the DOS also has exponential character, but the DOS itself is not the cause of Urbach tail.

Based on the experimental results, the current assumption is that the Urbach tails in amorphous semiconductors are caused by both thermal effects and static disorder [23]. Hence it can be concluded that, in the lower
Optical absorption in amorphous semiconductors

temperature region, the occurrence of Urbach tail may be considered to be primarily from the structural disorders. As temperature increases, the thermal vibrations become active and the associated thermal disorders due to atomic vibrations also contribute to the exponential absorption. Once a sample is prepared and annealed, the structural disorders may not vary, however, as the temperature increases high enough the effect of structural disorders may be overtaken by that of thermal disorders. The temperature at which such an overtaking occurs is called the fictive temperature, above which the influence of structural disorders on the absorption spectrum becomes relatively negligibly small.

1.6.3 Far infrared absorption

In a crystalline solid, the lattice vibrational excitations are plane waves characterised by wave vector $\vec{k}$ as well as frequency $\nu_{ph}$. Each mode of excitation is termed a phonon, and the $\nu_{ph}(\vec{k})$ phonon dispersion relations provide an energy-versus-momentum representation of the vibrational modes which is analogous to the $E(\vec{k})$ band structure representation of the crystals electronic states. In an amorphous solid, the vibrational modes are no longer plane waves (and $\vec{k}$ has no meaning), but continue to use phonons as a convenient abbreviation for the vibrational elementary excitations of the solid. While $\nu_{ph}(\vec{k})$ is not a valid concept in an amorphous solid, the concept of a vibrational density of states $N_v(\nu)$ retains its validity [25].

In the case of phonon excitations in crystalline solids, as a consequences of $\vec{k}$ conservation, of the $10^{24}$ phonon modes that exists in a typical macroscopic sample, only a few posses the privilege of interacting with light. Whereas, in an amorphous solid, all phonons may participate in interactions with light [25].
1.7 Electronic transport in amorphous materials

1.7.1 Carrier transport in a rigid lattice

In a rigid network of atoms in an amorphous solid, electrons (holes) are assumed to move through the conduction extended-states (valence extended states) and/or through the localized states without being subjected to the lattice vibrations. Therefore, the electron-phonon coupling can be ignored in this case. The electronic configuration of individual atoms in a solid remains the same in both crystalline and amorphous solids. However the atomic configurations in amorphous solids are different from crystalline solids, because of the absence of long-range orders in the former. On the basis of the tight-binding approach, regardless of the lack of long-range orders, a fully coordinated atomic network of amorphous solids is expected to offer crystalline-like behavior to the transport of charge carriers [4]. An electron spends an equal amount of time on each of the two-bonded atoms. Thus such networks give rise to the extended states and therefore the transport of charge carriers in the conduction and valence extended states of amorphous solids is basically the same as that of charge carriers in the conduction and valence bands of crystalline solids. However, one can expect the effective mass of a charge carrier to be different in an amorphous solid from that in a crystalline solid. The density of states in the region of extended states deviates little from that in the band regions of crystalline solids and is given by the density of the free electron states. In which case it is proportional to the square root of the energy. It is the presence of tail states and dangling bond states in amorphous solids that makes them behave different from its crystalline form. Both tail states and dangling bond states are localized states and transport of charge carriers in these states at low temperatures
can only be described by quantum tunneling from one site to another. The border between the extended states and localized states is called the mobility edge. According to Mott, the zero-temperature electronic transport should vary discontinuously with energy at the mobility edge (leading to the famous term, *minimum metallic conductivity*) [26].

### 1.7.2 Band conduction in non-degenerate state

The nature of the transport of charge carriers gets altered when a charge carrier crosses the mobility edges $E_C$ and $E_V$. The transport above $E_C$ is the band conduction type for electrons and transport below $E_V$ is band conduction type for holes. Transport through localized states is called the hopping conduction. The electronic transport at relatively high temperatures (near room temperature) in amorphous solid is believed to occur in the extended states. For electrons this yields an activation-type temperature dependence for the conductivity as

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$  \hspace{1cm} (1.11)

where $\Delta E = E_C - E_F$ is called the activation energy and is the separation of $E_F$ from the mobility edge $E_C$ and $\sigma_0$ is the pre-exponential factor.

### 1.7.3 Hopping conduction

The term hopping conduction means that localized electrons jump (diffuse) quantum mechanically from site to site. The mechanism of hopping conduction was first discussed in doped semiconductors [27, 28] and was then extended to amorphous semiconductors [29]. The hopping may be
assisted by phonons and hence phonon-assisted hopping between sites will be treated in this section.

In Mott’s formalism, the hopping process is simplified by assuming that the dominant contribution to the hopping current is through states within $k_B T$ of the chemical potential $\mu$, thereby eliminating the exact occupation probabilities of the states in the description [29]. In this case the hopping probabilities ($P_{ij}$) are the probability of a carrier tunnelling from a localized state $i$ with energy $E_i$ to an empty state $j$ with energy $E_j$:

$$P_{ij} \approx \begin{cases} \exp \left( -2\alpha R_{ij} - \frac{E_i - E_j}{k_B T} \right) & \text{if } E_j > E_i \\ \exp(-2\alpha R_{ij}) & \text{if } E_j \leq E_i \end{cases}$$

(1.12)

with $R$ the physical distance separating the two localized states, and $\alpha$ the localization parameter of these states. In a one-dimensional system the $\alpha$ parameter corresponds with the exponential decay of a wave function in a potential barrier and is directly related to the height of the potential barrier. In systems of higher dimensions this relation is less obvious, and the $\alpha$ parameter is characterised by an integration of all possible tunnelling paths between two sites. That is, the $\alpha$ parameter reflects the ‘potential landscape’ surrounding the hopping sites.

In this description, the approximation $|E_i - E_j| \geq k_B T$ is used, although the validity of this approximation is questioned by several authors [30, 31].

**Nearest-neighbour hopping (NNH)**

Since the hopping probability depends on both the spatial and energetic separation of the hopping sites, it is usually described the hopping processes in a four-dimensional hopping space, with three spatial coordinates and one energy coordinate. In this hopping space a range $R$ is defined as
Electronic transport in amorphous materials

\[ R_{ij} = -\ln(P_{ij}) \] (1.13)

This range, given by the magnitude of the exponent in equation 1.12, represents a distance in four-dimensional hopping space, indicating the hopping probability. In a system in which localized states are randomly distributed in both position and energy, the probability distribution function of all hops originating from one site is generally dominated by the hop to the nearest neighbouring site in the four-dimensional hopping space, due to the exponential character of the hopping probabilities. This site at closest range corresponds only with the spatially nearest neighbour if the first term on the right hand side of equation 1.12 is dominant. This is true if \( \alpha R_0 \gg 1 \), with \( R_0 \) the average spatial distance to the nearest neighbouring empty localized state. That is in cases of strong localization and/or low concentration of localized states, the hopping distance \( R \) is limited to the spatial nearest neighbouring hopping site at average distance \( R_0 \), and the corresponding conduction mechanism is called nearest neighbour hopping (NNH, see figure 1.12).

Variable range hopping (VRH)

If \( \alpha R_0 \) is in the order or less than unity, or in all cases at sufficiently low temperatures, the second term on the right hand side of equation 1.12 contributes significantly to the hopping probability and hops to sites that are further away in space but closer in energy might be preferable. This is the variable range hopping (VRH) process, introduced by Mott (Figure 1.13).

The DC hopping conductivity can be expressed as
Figure 1.12: Schematic representation of nearest neighbour hopping.

Figure 1.13: Schematic representation of variable range hopping.
Electronic transport in amorphous materials

\[
\sigma = \sigma_0 \exp \left( \frac{T_0}{T} \right)^{\frac{1}{4}} \tag{1.14}
\]

with

\[
T_0 = C_T \frac{\alpha^2}{k_B N_F} \tag{1.15}
\]

proportionality constant \( C_T \) is given by \( C_T = \frac{24}{\pi} \) and

\[
\sigma_0 = \nu_{ph} \left( \frac{N_F}{\pi\alpha k_B T} \right)^{\frac{1}{2}} \tag{1.16}
\]

Large discrepancy is found between the experimental and theoretical values of pre-exponential factor \( \sigma_0 \) in most amorphous semiconductors [32, 33] and VRH theory is still considered incomplete [4]. Band conduction in degenerated state is described in section 1.8.2 while discussing the transparent amorphous semiconductors.

1.1.4 Hall Effect

The basic transport properties usually measured in crystalline semiconductors are the conductivity \( \sigma \) and Hall coefficient \( R_H \). For \( n \)-type semiconductors the \( R_H \) is negative (positive for \( p \)-type) and is given by the general formula

\[
R_H = -\frac{r}{nq} \tag{1.17}
\]

where, \( r \) is the scattering factor, \( q \) is the electric charge and \( n \) is the electron density. From \( \sigma \) and \( R_H \), we get the Hall mobility as \( \mu_H = |R_H|\sigma \). This interpretation of hall coefficient is valid for materials in which the mean free path is large compared with the interatomic spacing [34].
The most anomalous behavior in the carrier transport in amorphous semiconductor is that the Hall effect has the opposite sign estimated from the thermoelectric power. It is called as $pn$ anomaly; holes give a negative sign and electrons positive in the Hall voltage. However, there is no sign anomaly in degenerate amorphous semiconductors in which electronic transport occurs well above the mobility edge (discussed in section 1.8). When carrier transport occurs near mobility edge, the mean free path is expected to be very small and corresponds to the interatomic spacing. As a consequence, the standard transport theory based on the Boltzmann equation is not useful.

Applying the concept of hopping polarons developed by Friedman and Holstein [35], Friedman [36] has put forward a theory for the Hall effect for carriers moving in amorphous solids near the mobility edge. It produces interference between two scattering paths involving three atomic sites A, B and C. One path is from A to B direct and the other from A to B via C. The Hall mobility deduced in this way is found to be independent of temperature and in qualitative agreement with the observations, but the Hall coefficient is always found to be negative whether the carriers are electrons or holes. This has been interpreted as Friedman’s theory being correct only in predicting the $n$-type Hall coefficient for $p$-type material but not the $p$-type Hall coefficient for $n$-type material.

For explaining the behavior of $n$-type a-Si:H, Emin has suggested a theory by considering that carriers form polarons located on Si-Si bonds [37]. Emin’s theory requires that the odd order close loops must be predominant in the structure, because the orbital on each bond is antibonding so that the wavefunction changes sign at each hop. Although polarons are not formed in crystalline silicon, Emin has suggested that they can be formed...
in amorphous silicon due to its softened structure. The observed activation 
energy in the mobility is then attributed to the polaron hopping. However, 
Emin's theory is not widely accepted, because it demands on the electron 
to move from one bond to an adjacent bond, around an odd numbered ring, 
which is not always possible in any amorphous structure.

Mott has suggested that the positive Hall coefficient for n-type silicon 
can be explained without any assumption of odd-numbered paths, if the 
centers which scatter electrons are considered to be the stretched Si-Si 
bonds [38]. Such stretched bonds have electron energies different from the 
majority of the bonds. Extending then Friedman's theory to such stretched 
bonds as scattering centers, the interference between two paths, AB and 
ACB, can lead to a change in the sign of the electronic wavefunction.

Applying a perturbative renormalization-group procedure, Okamoto et 
al. [39] have studied the behavior of weak field Hall conductivity near the 
mobility edge and found that the anomalous sign in the Hall coefficient 
can occur if the mean free path of carriers is shorter than a critical value. 
Accordingly, the microscopic Hall conductivity changes its sign near but 
above the mobility edge and hence the Hall coefficient also changes its sign. 
A quantum interference effect of electron transport near the mobility edge 
has been taken into consideration, which is also taken into account in a 
metallic conduction regime. The Hall mobility against the carrier mean 
free path is deduced. This is also consistent with the observation no sign 
anomaly in degenerate amorphous semiconductors [40].

1.7.5 Doping in amorphous semiconductors

Generally, transparent conductors show their highest conductivity in its 
crystalline phase. They are also very conductive in its amorphous state and
can achieve electron mobilities of 10 to 40 $\text{cm}^2/\text{Vs}$. Anderson suggested that disorder can cause a localization of electron states in the band structure [41]. Mott and Davis showed that disorder first localizes states at the band edges, and that the extended states and localized tail states were separated by an energy called the mobility edge. As the disorder increases, the mobility edge move further into the bands and eventually whole band becomes localized.

In pure amorphous silicon, there is large density of band gap states, which makes this material electronically dirty. The addition of hydrogen to this has the effect of cleaning out the undesirable band gap states. Hydrogen terminates (bonds to) the dangling bonds, removing the gap states associated with this native defect. Hydrogen opens up the weak reconstructed bonds associated with the voids and bonds to those Si atoms as well, replacing each such long Si-Si bond by two Si-H bonds. Since the Si-H bond is very strong and its bonding-antibonding splitting is larger than that of Si-Si, the states introduced by the Si-H bonds lie at energies which are outside of the band gap region of the a-Si host. In case of a-Si:H, bonds are sp$^3$ states, but states around its band gap are p states. The valence band maximum (VBM) consists of pure p states, whereas the conduction band minimum (CBM) consists of mixed s, p states. The Si-Si bond length is relatively fixed in a-Si:H, but the bond angle $\theta$ varies by 10° and the dihedral angle $\phi$ varies by 180°. The $\phi$ is a strong source of disorder in the valence band edge and causes a strong tailing of the valence band edge. Conduction band is less affected by dihedral angle disorder, but it is affected by bond angle disorder. This bond angle fluctuation gives quite strong tailing in conduction band edge, but less than for the valence band edge.
Electronic transport in amorphous materials

$\text{Donor level}$

$\text{Defect level}$

$\text{Fermi level}$

$\text{Occupation:50\%}$

$\text{New dangling bond states}$

Figure 1.14: Doping of an amorphous network of Si atoms by a P atom. Band diagram of undoped and doped a-Si is also shown. The increased occupancy of the dangling bond level raises the Fermi energy.

Doping in a-Si:H is not quite the same as in crystalline Si. In crystalline materials, doping occurs by substituting impurity atoms. The surrounding semiconductor network imposes its bonding configuration upon the impurity atoms, which in the case of an acceptor is then one electron short of full valence or in the case of donor has one electron more than full valence. The former situation produces an acceptor electron energy level just above the valence band that is easily ionized to produce a free hole in the valence band, while the latter situation produces a donor level just below the conduction band that is easily ionized to produce a free electron in the conduction band [42].

If an impurity is added to an amorphous semiconductor, there is no constraint on the number of bonds that the impurity will form. For exam-
Amorphous Semiconductors and Amorphous Oxide TFTs

For example, if phosphorous were to be added to a-Si:H, the local Si network should adjust so that only the three bonds required by the phosphorous for perfect coordination would form. It might be expected, therefore, that amorphous semiconductors cannot be doped. However, Spear and LeComber demonstrated both p-type and n-type doping in a-Si:H by the so called “Street Mechanism” [43]. In this process, most of the dopant impurities will form the expected number of bonds according to their ideal coordination. For example, in the case of phosphorous, three bonds will be formed and the P will be neutrally charged (P$_3^0$ state). However, it requires only 0.5 eV for the P atom to form four bonds (P$_4^0$ state) (This doping site is always ionized so it is P$_4^+$). In the presence of a weak Si-Si bond, this energy may be recovered by breaking the weak bond to form a dangling bond. At the same time an electron is then transferred from the P atom to the dangling bond, which is then negatively charged (Si$_3^-$ state). Thus doping is expressed by the equilibrium reaction, P$_3^0 + Si^0_4 = P^+_4 + Si^-_3$. As a result of this process, a higher proportion of the dangling bond defects in the mobility gap are negatively charged and the Fermi level rises to accommodate this change and the material is doped n-type [42]. Similarly in p-type doping, the dangling bonds becomes positively charged, and the Fermi level shifts towards the valence band. However, above equilibrium pins the Fermi energy $E_F$ below the donor level, and thus doping in a-Si:H never moves $E_F$ above the CB mobility edge.

1.7.6 Advantages of amorphous materials over poly-crystalline materials

Use of amorphous materials in devices helps to overcome the complexities and limitations of the use high substrate temperature during thin film depo-
sition. Since amorphous materials are not subjected to any selection rules, optical absorption is higher compared crystalline materials (see section 1.6). In solar cell applications, this property helps to reduce the thickness of the absorbing layer required to produce considerable light absorption compared to crystalline silicon. In other words, use of a-Si layer consumes less material to get the same absorption as that of a crystalline silicon device. Hence the product cost will be less in this case.

Materials with tunable energy gaps find a variety of applications in optoelectronic technologies. Crystalline Mg\textsubscript{x}Zn\textsubscript{1-x}O alloy has a band gap tunability over the range 3.3 - 3.99 eV by adjusting the Mg content [44, 45]. However, crystal phase segregation between ZnO and MgO was observed for Mg concentrations \( x \geq 36\% \), due to different crystal structures and large lattice mismatch between ZnO and MgO [46]. Similarly BeZnO alloys also have a large band gap tunability but still shows problems with lattice mismatch between ZnO and BeO [47, 48]. The problems of the crystal phase segregation between the components of a crystalline alloy and the lattice mismatch between film and substrate can be avoided by growing an amorphous structure of the considered alloy [49, 50].

Polycrystalline oxides like ZnO have columnar grain structures even at room temperature (RT) deposition. Thin film transistors (TFTs) with polycrystalline oxide channel suffer from problems associated with the grain boundaries [51, 52] such as the instability to the atmosphere by the gas absorption/desorption into the grain boundaries; higher film surface roughness because of facet formation etc. amorphous oxides have uniform structures and smoother surfaces which could yield smooth channel interfaces to the gate insulators.
1.8 Transparent amorphous oxide semiconductors

1.8.1 Conductivity mechanism in transparent oxide semiconductors

Today, optoelectronic materials research are mainly directed to oxide semiconductors as many of them are non-toxic and abundant in nature. This overcomes serious resource and environmental issues which the modern industry are facing. In transparent oxide semiconductors (TOSs), a highly dispersed band at the bottom of the conduction band provides the high mobility electrons (due to their small effective masses) and low optical absorption due to a pronounced Burstein-Moss shift which helps to keep intense interband transitions out of the visible range. However, the interband transitions from the partially occupied band at the top of the conduction band prevents from achieving the 100% transparency in the visible range in the conventional TOSs.

Origin of conductivity in TOSs is generally related to the oxygen vacancies and cation interstitials. It has been postulated for a long time that the conductivity of transparent materials is related to the existence of shallow donor levels near the conduction band, formed by oxygen vacancies [53]. Medvedeva et al. [54] attributed the high conductivity of indium tin oxide (ITO) to the presence of shallow donor or impurity states located close to the host (In$_2$O$_3$) conduction band. This donor or impurity band is produced via chemical doping of Sn$^{4+}$ for In$^{3+}$ or by the presence of oxygen vacancy impurity states in In$_2$O$_{3-x}$. The excess or donor electron undergoes thermal ionization at room temperature into the host conduction band which ultimately leads to a degenerate gas of electrons in the conduction band. At the same time the fundamental host band gap is left intact, i.e.
the electrically conductive material remains optically transparent in the visible region.

In contrast, there are reports which show that oxygen vacancies form deep levels [55, 56]. First-principles calculations of formation energies and electrical (donor, acceptor) levels for various intrinsic defects (oxygen vacancy $V_O$, tin interstitial $Sn_i$, tin antisite $SnO$, tin vacancy $V_{Sn}$, oxygen interstitial $Oi$) in different charge states and under different chemical potential conditions in $SnO_2$ indicate that $Sn_i$ plays a more prominent role than that of $V_O$. They inferred the following:

1. While oxygen vacancy produces a level inside the band gap, owing to its loosely bound outer electrons interstitial Sn produces a donor level inside the conduction band, leading to instant donor ionization and conductivity.

2. $Sn_i$ has a very low formation energy.

3. The presence of $Sn_i$ lowers the formation energy of $V_O$, explaining the natural oxygen deficiency and overall non-stoichiometry of $SnO_2$.

4. The absence of inter-conduction band absorption is a consequence of a special feature of the band structure of $SnO_2$, manifesting a large internal gap inside the conduction band that eliminates optical transitions in the visible range.

In addition to the general features of an oxygen vacancy model, these results reveal the important role of tin interstitial. They showed that $Sn_i$ and $V_O$ produce shallow donor levels which explains n-type conduction in undoped $SnO_2$. The electrons released by $Sn_i$ and $V_O$ are not compensated owing to the absence of spontaneous formation of acceptor like intrinsic
defects ($V_{Sn}$ and $O_i$), and do not make direct optical transitions in the visible range due to a large gap between the Fermi level and the energy level of first unoccupied states.

Similar studies on ZnO shows that [57]:

1. The zinc interstitial Zni form a shallow donor level, supplying electrons since its formation enthalpy is low for both Zn-rich and O-rich conditions and native compensating defects of Zni (i.e., $O_i$ or $V_{Zn}$) have high formation enthalpies at the Zn-rich conditions so these electron killers are rare.

2. Since the defects that compensate p-type doping ($V_O$, Zni) have low formation enthalpies at both Zn rich and O-rich conditions, ZnO cannot be doped p type via native defects ($O_i$, $V_{Zn}$) (even though they form shallow acceptor levels).

In general, even though the contributions of metal interstitials are acknowledged, the oxygen vacancy model is still using to explain the observed conductivity behaviour in TOSs.

1.8.2 Transparent amorphous oxide semiconductors

Amorphous semiconductors have generally been classified in two categories: a tetrahedral system (represented by a-Si:H) and a chalcogenides system (such as a-$As_2S_3$). However neither system possesses both high transparency to visible radiation and high conductivity because of their small band gaps or small mobilities.

Low mobility in conventional amorphous materials causes great difficulty in obtaining transparent amorphous semiconductors. For instance,
the value of mobility in a-Si:H is of the order of $10^{-3} \text{cm}^2/\text{V}s$, which is smaller by ~3 orders of magnitude than that in polycrystalline Si. Although amorphous semiconductors based on transition metal oxides such as $V_2O_3$ have been extensively studied, low mobility ($\sim 10^{-4} \text{cm}^2/\text{V}s$) and intense colouring make them less interest in transparent electronics.

Since the mobility is proportional to the width of the conduction bands, a large overlap between relevant orbitals is required to achieve high mobility in amorphous semiconductors. In addition, the magnitude of the overlap needs to be insensitive to the structural randomness which is intrinsic to the amorphous state. Metal oxides composed of heavy metal cations (HMCs) with an electronic configuration $(n-1)d^{10}ns^0$ (with $n \geq 4$) satisfy these requirements [58-60]. In amorphous oxide semiconductors, spatial spreading of the $ns$ orbital is large and the overlap between these $ns$ orbitals with spherical symmetry is large and insensitive to any angular variations in the M-O-M bonds (where M is a metal cation) compared with p-p or d-p orbitals having high anisotropy in geometry. Oxide systems have a large bandgap because of low energy of O 2p orbitals, which constitute the top of the valence band. The bottom part of the conduction band in these oxides is primarily composed of $ns$ orbitals of HMCs. These are the major reasons for the large mobility and finite Hall voltage observed in these materials. Unlike the case of a-Si:H, these amorphous oxides does not show any anomaly in Hall voltages.

Double oxides are preferred over single oxides with respect to formation of an amorphous state. As the thickness of the active layers used to fabricate TFT is in general below 100 nm, the final device performances are highly dependent on the density of surface states and its morphology. So,
highly smooth surfaces are easily obtained when the films are amorphous [61, 62].

In contrast to crystalline solids, oxides have strong ionicity and CBM and VBM are usually formed by different ionic species. When metal atoms and oxygen atoms come close, charge transfer occurs due to large differences in electron affinity and ionization potential, which ionizes these atoms. The ions form negative electrostatic potential at the cationic sites and positive potential at the anionic sites (Madelung potential), which consequently stabilizes the ionized states in the crystal structure (Figures 1.15 and 1.16). Therefore CBMs are mainly made of the metal cation and VBMs of oxygen 2p orbitals in typical oxides (these are not the cases for transition metals,
lanthanide and actinide as their $d$ and $f$ orbitals may locate near VBM or in the bandgap). Main group oxides have large bandgaps because the large Madelung potential increases the energy splitting. For TCOs such as SnO$_2$ and ITO, CBMs are mainly made of s orbitals with a large principle quantum number $n$ (e.g., $n = 5$ for Sn and In). These s orbitals have large spatial size and form large hybridization even with second neighbor metal cations. This is the reason why TCOs have small electron effective masses. Such oxides can be good electrical conductors as long as high density carrier doping is possible [63].

In transparent amorphous oxide semiconductors (TAOSs), the conduction band minimum state is highly localized on the metal s states and its energy depends mainly on the interaction between second neighbour metal sites ($V(ss)$), and not much on the interaction between metal s and oxygen p states ($V(sp)$). The Slater-Koster interaction $V(l, m)$ between orbitals on atoms $l$ and $m$ would depend on their distance ($r$), the angles $\theta$ between the orbitals and separation vector $r$, and their dihedral angle $\phi$ [64],

$$V(l, m) = V(r, \theta, \phi)$$  \hspace{1cm} (1.18)

Because of the spherical symmetry, the interaction between two s states reduces to,

$$V(ss) = V(r)$$  \hspace{1cm} (1.19)

Hence the only source of disorder is the variation of the metal-metal distance, and any angular disorder has no effects on s states. In contrast to covalent bonded amorphous semiconductors, in TAOSs, the Fermi level
can be moved into the conduction band, creating large free carrier concentrations [60]. Since aliovalent dopants does not produce deep gap states in TAOSs, there are no localized states at the conduction band edge [57, 65]. Hence even in binary and ternary oxide systems, the conduction band edge is still delocalized and is not affected by compositional disorder. In case of simple oxides like ZnO, electrical conduction mechanism is controlled by oxygen vacancies and metal interstitial. Whereas for binary oxides, the the number of metal ions and their state of oxidation, together with oxygen vacancies and defects control the electrical conduction [66].

In a-Si:H, H acts as a key catalyst of bond breaking and rearrangement and hence it suffers from instabilities, called Staebler-Wronsky effects in solar cells and bias-stress instability in TFTs [67-70]. These instabilities can never really be removed in a-Si:H; their effects can be minimised by good design. In TCOs and TAOSs, hydrogen can exist, but it is present as ionized H⁺ sites [71]. Atomic H lies next to an O²⁻ site and forms an OH⁻ ion releasing an electron. In this configuration, H is not able to catalyse bond rearrangements.

1.8.3 Electronic structure of amorphous oxide semiconductors

Structural disorder in amorphous semiconductors make it very difficult to study the electronic structure of amorphous semiconductors. Narushima et al. [72] performed ultraviolet photoelectron (PE) and ultraviolet inverse photoelectron (IPE) spectroscopic studies on amorphous cadmium germanate to observe the DOS of the valence band and conduction band, respectively. There was no substantial difference in the DOS with respect to the energy distribution at the conduction band bottom between the
amorphous and the crystalline states. The extended nature of the states at the conduction band bottom results comparable electron mobility and effective mass in the amorphous phase as those of the polycrystalline form. The magnitude of the overlap between neighboring Cd 5s orbitals was insensitive to the neighboring Cd-Cd distance which results large dispersion of the conduction band even in the amorphous state. The topological sequence of the ion arrangement did not show much influence on the electronic properties as the conduction band bottom is primarily composed of vacant s orbitals of the metal cations.

1.9 Amorphous thin film devices

The first major application of amorphous semiconductors was in the filed of Xerography [73]. This process utilizes generally the photoconductivity of amorphous selenium films. Xerox Corporation has developed colour copier employing different layers of amorphous chalcogenides. Some of the earlier application of amorphous chalcogenide materials include the development of Ovonic threshold switch and Ovonic memory switch [3]. The switching refers to a rapid change in the electrical conductivity of the amorphous chalcogenide material when the applied field reaches of the order of $10^5 \text{ V/cm}$. In memory switching, high conductivity state is retained even after the applied voltage is removed. Rectifying junctions have been fabricated by sputtering amorphous silicon (a-Si) onto crystalline Si substrates [74]. TFTs have been constructed with vacuum deposited a-Si as the semiconductor on single crystalline silicon substrates with 3000 Å SiO$_2$ layer [75]. Because of large density of localized states in a-Si, these devices exhibit large threshold voltages ($V_T > 50 \text{ V}$).
First report on hydrogenated amorphous silicon (a-Si:H) appeared in 1969 [76]. Thereafter an amorphous $p-n$ junction has been fabricated by Spear et al. [77] and photovoltaic properties by Carlson et al. [78]. Zanzucchi et al. [79] constructed a photoconductivity cell using a-Si:H in 1977. Electroluminescence was detected in a forward biased a-Si:H diode [80]. Using the property of reversible, light induced conductivity changes in a-Si:H [81], the concept of optical storage was given by Staebler [82]. A field-effect type device was fabricated by Spear et al. [83] using a thick glass substrate as insulator to study the DOS in a-Si:H. In a later work, a thin film of amorphous Si$_3$N$_4$ was used as the insulating layer [84]. L. A. Goodman has successfully fabricated a-Si:H TFTs using a metal-oxide-semiconductor (MOS) structure with SiO$_2$ insulator [73].

1.10 Literature review on thin film transistors with transparent oxide semiconductor channels

Transparent amorphous semiconductor based TFTs have recently been investigated by several research groups. Devices fabricated from oxide semiconductor channel TFTs have relatively high mobilities despite their amorphous nature. This session gives a detailed review of TFTs using a wide bandgap oxide channel layer. The basic device structure, its working and characterisation is given in session 2.3 in the next chapter.

In 1996, Prins et al. [85] reported a field-effect transistor made of transparent oxide thin films, showing an intrinsic memory function due to the usage of a ferroelectric insulator. The device consists of a high mobility Sb-doped n-type $SnO_2$ semiconductor layer, $PbZr_{0.2}Ti_{0.8}O_3$ as a ferroelectric insulator, and $SrRuO_3$ as a gate electrode, each layer prepared by pulsed
Laser deposition. This report focuses on the ferroelectric nature of the device and there was no mention about the electrical parameters of the TFT. Here the optical transparency of the TFT was limited by the gate electrode $SrRuO_3$. Following this, J.B. Giesbers et al. [86] of Philips research laboratory reported an all oxide transparent thin film memory transistor using a 10 nm n-type SnO$_2$:Sb semiconductor channel with a 10 nm BaZrO$_3$ capping layer, In$_2$O$_3$:Sn contact pads, a 250 nm PbZr$_{0.2}$Ti$_{0.8}$O$_3$ layer as a ferroelectric insulator, and conducting SrRuO$_3$ as gate electrode. This reports an on-off ratio greater than $10^3$. In 1998, Takatsui et al. [87] reported the fabrication of sputter deposited amorphous indium zinc oxide (a-IZO) thin films on LCD grade glass substrate and their application to TFT.

Over the last few years, much interest has been shown in the development of TFTs with wide band gap semiconductor channel layers. Among the various types of channel layer materials, amorphous oxide semiconductors (AOSs) appear promising, especially when we consider the factors of large area deposition on flexible substrates and their mechanical stability. Present day large area LCD technology uses TFTs that have been fabricated on glass substrates. The fragile nature of glass impose a finite limit on the thickness reduction of the substrate. The substrates and their protecting bodies occupy the greater part of the electronics in volume and determine their total weight. Use of non-fragile soft substrates, like plastics and metal foils, in TFT fabrication helps to get rid of much of these problems. Such an approach limits the processing temperature because of their higher thermal expansion coefficients. Although organic TFTs (OTFTs) have been widely studied for years for this purpose, they are still facing the stability problems and facing much lower saturation mobility values.
In recent years, AOS TFTs emerged as an alternative to overcome much of these problems.

Several amorphous wide bandgap semiconductor materials like zinc oxide, indium gallium zinc oxide, zinc tin oxide, gallium nitride, and zinc indium oxide have been employed as TFT n-channel layers in recent years. The recent development in the area of TFTs using wide band gap semiconductors are summarized in the tables 1.1-1.6. Various parameters like mobility, threshold voltage, on-off ratio, subthreshold swing etc are shown in the tables. Table 1.1 shows the ZnO based thin film transistors using different types of source, drain, gate electrodes and gate insulators.

Following convention is used in the tables 1.1-1.6.

$\mu_{fe}$: field effect mobility, $\mu_{sat}$: saturation mobility
$\mu_I$: Incremental mobility, $\mu_{PI}$: Peak incremental mobility
$V_{ON}$: Turn on voltage, S-D: Source-Drain
Sub: Substrate, S: Subthreshold slope, Ref: Reference
Sub/annealing temp.: Substrate temperature or annealing temperature
RT: Room temperature, RTA: Rapid thermal annealing
RF: Radio frequency, PLD: Pulsed laser deposition
CBD: Chemical bath deposition
ALD: Atomic layer deposition
PECVD: Plasma enhanced chemical vapour deposition
RF-PERTE: RF plasma enhanced reactive thermal evaporation
Table 1.1: Properties of ZnO based thin film transistors: Performance parameters

<table>
<thead>
<tr>
<th>Channel layer</th>
<th>S-D electrode</th>
<th>Gate electrode</th>
<th>Insulator</th>
<th>Sub layer</th>
<th>Mobility ( (cm^2/Vs) )</th>
<th>On-Off ratio ( (V) )</th>
<th>Threshold voltage ( (V) )</th>
<th>S Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>-</td>
<td>Ta</td>
<td>a-SiN</td>
<td>-</td>
<td>( \mu_f=7 )</td>
<td>-</td>
<td>-</td>
<td>[88]</td>
</tr>
<tr>
<td>ZnO</td>
<td>GZO</td>
<td>ITO</td>
<td>ATO</td>
<td>Glass</td>
<td>( \mu_{sat}=27 )</td>
<td>10^5</td>
<td>19</td>
<td>1.39 [89]</td>
</tr>
<tr>
<td>ZnO</td>
<td>ITO</td>
<td>ITO</td>
<td>ATO</td>
<td>Glass</td>
<td>( \mu_{eff}=2 - 5 )</td>
<td>10^7</td>
<td>-</td>
<td>- [90]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Ti - Au</td>
<td>Ti - Au</td>
<td>SiO(_2)</td>
<td>n-Si</td>
<td>( \mu_f=2 )</td>
<td>10^6</td>
<td>-</td>
<td>- [91]</td>
</tr>
<tr>
<td>ZnO</td>
<td>In</td>
<td>Cr</td>
<td>SiO(_2)</td>
<td>SiN(_x)</td>
<td>Glass</td>
<td>( \mu_f=0.031 )</td>
<td>10^5</td>
<td>2.5</td>
</tr>
<tr>
<td>ZnO</td>
<td>ZnO:Ga</td>
<td>ITO</td>
<td>SiO(_2)</td>
<td>SiN(_y)</td>
<td>Glass</td>
<td>( \mu_f=70 )</td>
<td>10^5</td>
<td>1.8</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>SrTiO(_3)</td>
<td>( \mu_f=30 )</td>
<td>10^6</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>Ni</td>
<td>Mo</td>
<td>Ta(_2)O(_5)</td>
<td>Glass</td>
<td>( \mu_f=0.1 )</td>
<td>10^5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>Al</td>
<td>Cr</td>
<td>BZN</td>
<td>Glass</td>
<td>( \mu_{sat}=1.13 )</td>
<td>10^4</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>ITO</td>
<td>ITO</td>
<td>SiO(_2)</td>
<td>Glass</td>
<td>( \mu_{sat}=0.248 )</td>
<td>10^5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>a-ZnO</td>
<td>ITO</td>
<td>ITO</td>
<td>SiN</td>
<td>Glass</td>
<td>( \mu_{sat}=25 )</td>
<td>10^7</td>
<td>4.53</td>
<td>1.24</td>
</tr>
<tr>
<td>a-ZnO</td>
<td>-</td>
<td>-</td>
<td>Al(_2)O(_3)</td>
<td>-</td>
<td>( \mu_{sat}=4 )</td>
<td>10^6</td>
<td>2.63</td>
<td>1.82</td>
</tr>
<tr>
<td>ZnO:N</td>
<td>-</td>
<td>-</td>
<td>Al(_2)O(_3)</td>
<td>-</td>
<td>( \mu_{sat}=6.7 )</td>
<td>10^7</td>
<td>4.1</td>
<td>0.67 [99]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Ti - Pt</td>
<td>ITO</td>
<td>SiN</td>
<td>Glass</td>
<td>( \mu_f=0.5 )</td>
<td>10^2</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Au</td>
<td>-</td>
<td>-</td>
<td>( \mu_f=8 )</td>
<td>10^6</td>
<td>-</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Table 1.1: ....continued

<table>
<thead>
<tr>
<th>Channel layer</th>
<th>S-D electrode</th>
<th>Gate electrode</th>
<th>Insulator</th>
<th>Sub</th>
<th>Mobility ($cm^2/Vs$)</th>
<th>On-Off ratio</th>
<th>Threshold voltage (V)</th>
<th>S ($V/dec$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>ITO</td>
<td>Al</td>
<td>Al$_2$O$_3$</td>
<td>Glass</td>
<td>$\mu_{fe}=0.8$</td>
<td>$10^7$</td>
<td>8</td>
<td>1.5</td>
<td>[101]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Ag</td>
<td>Ag</td>
<td>ZnMgO</td>
<td>p-Si</td>
<td>$\mu_{fe}=20$</td>
<td>$10^4$</td>
<td>-</td>
<td>-</td>
<td>[102]</td>
</tr>
<tr>
<td>ZnO$_x$</td>
<td>Al</td>
<td>n$^+$Si</td>
<td>SiO$_2$</td>
<td>n$^+$Si</td>
<td>$\mu_{sat}=2-12$</td>
<td>$10^7$</td>
<td>-8 - 18</td>
<td>1.4</td>
<td>[103]</td>
</tr>
<tr>
<td>SnO$_{21-x}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>GZO</td>
<td>GZO</td>
<td>a-HfO$_2$</td>
<td>Glass</td>
<td>$\mu_{sat}=14.7$</td>
<td>$10^5$</td>
<td>2</td>
<td>-</td>
<td>[104]</td>
</tr>
</tbody>
</table>

BZN: Bismuth zinc niobate
Table 1.2: Properties of ZnO based thin film transistors: Preparation technique

<table>
<thead>
<tr>
<th>Channel deposition</th>
<th>Channel material</th>
<th>Sub/annealing temp. (°C)</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF magnetron</td>
<td>ZnO</td>
<td>RT</td>
<td>CaH₂fO₂ buffer layer between channel and insulator, bottom gate staggered</td>
<td>[88]</td>
</tr>
<tr>
<td>Sputtering</td>
<td>ZnO</td>
<td>-</td>
<td>poly-crystalline channel, bottom gated, TTFT</td>
<td>[89]</td>
</tr>
<tr>
<td>Ion beam sputtering</td>
<td>ZnO</td>
<td>ZnO RTA at 600 - 800° C</td>
<td>after ITO gate electrode deposition further RTA at 300° C, bottom gated, TTFT</td>
<td>[90]</td>
</tr>
<tr>
<td>RF magnetron sputtering</td>
<td>ZnO</td>
<td>Near RT</td>
<td>poly-crystalline channel, bottom gated TFT</td>
<td>[91]</td>
</tr>
<tr>
<td>PLD</td>
<td>ZnO</td>
<td>450</td>
<td>poly-crystalline channel, double oxide bottom gated TFT</td>
<td>[92]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>ZnO</td>
<td></td>
<td>poly-crystalline channel, bottom gated, TTFT</td>
<td>[93]</td>
</tr>
<tr>
<td>PLD</td>
<td>ZnO</td>
<td></td>
<td></td>
<td>[94]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>ZnO</td>
<td>230</td>
<td>poly-crystalline channel, bottom gated TFT</td>
<td>[95]</td>
</tr>
<tr>
<td>CBD</td>
<td>ZnO</td>
<td></td>
<td>Bismuth zinc niobate (BZN) insulator, bottom gated TFT</td>
<td>[96]</td>
</tr>
<tr>
<td>CBD</td>
<td>a-ZnO</td>
<td>PECVD at 200° C (for insulator)</td>
<td>bottom and top gated, amorphous ZnO by reduced channel thickness, amorphous channel, TTFT</td>
<td>[97]</td>
</tr>
<tr>
<td>ALD</td>
<td>ZnO:N</td>
<td>-</td>
<td>bottom gated TFT</td>
<td>[98]</td>
</tr>
</tbody>
</table>
Table 1.2: ....continued

<table>
<thead>
<tr>
<th>Channel deposition</th>
<th>Channel material</th>
<th>Sub/annealing temp. (°C)</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF sputtering</td>
<td>ZnO</td>
<td>200 °C</td>
<td>two different refractive index SiN(n=2.45 and n=1.85), PECVD (insulator), bottom gated TFT</td>
<td>[100]</td>
</tr>
<tr>
<td>DC sputtering</td>
<td>ZnO</td>
<td>200 °C</td>
<td>dry etching method, top gated TFT</td>
<td>[101]</td>
</tr>
<tr>
<td>DC sputtering</td>
<td>(ZnO)$_x$</td>
<td>550-700 °C</td>
<td>poly-crystalline channel, bottom gated TFT</td>
<td>[102]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>ZnO</td>
<td>500 °C</td>
<td>Combinatorial study, annealing at 600 °C gave best performance, best performance composition x=0.25 and 0.8, bottom gated TFT</td>
<td>[103]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>ZnO</td>
<td>500 °C</td>
<td>RTA 200-500 °C for 1 min for enhancing transmittance</td>
<td>[104]</td>
</tr>
<tr>
<td>Channel layer</td>
<td>gate electrode</td>
<td>Insulator</td>
<td>Sub electrode</td>
<td>Mobility On-Off ratio (V/dec)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------------</td>
<td>-----------</td>
<td>---------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>ZnO</td>
<td>ZnO</td>
<td>ITO</td>
<td>ATO</td>
<td>2</td>
</tr>
<tr>
<td>a-ZnO</td>
<td>ITO</td>
<td>GZO</td>
<td>ATO</td>
<td>2</td>
</tr>
<tr>
<td>InOx</td>
<td>InOx</td>
<td>SiO2</td>
<td>ATO</td>
<td>2</td>
</tr>
<tr>
<td>a-InOx</td>
<td>ITO</td>
<td>SiO2</td>
<td>ATO</td>
<td>2</td>
</tr>
<tr>
<td>SnO2</td>
<td>SnO2</td>
<td>ITO</td>
<td>ATO</td>
<td>2</td>
</tr>
<tr>
<td>a-SnO2</td>
<td>ITO</td>
<td>ATO</td>
<td>ATO</td>
<td>2</td>
</tr>
<tr>
<td>ZTO</td>
<td>ZTO</td>
<td>ATO</td>
<td>ATO</td>
<td>2</td>
</tr>
<tr>
<td>a-ZTO</td>
<td>a-ZTO</td>
<td>ATO</td>
<td>ATO</td>
<td>2</td>
</tr>
<tr>
<td>ZIO</td>
<td>ZIO</td>
<td>Al</td>
<td>Al</td>
<td>2</td>
</tr>
<tr>
<td>a-ZIO</td>
<td>Al</td>
<td>Al</td>
<td>SiO2</td>
<td>2</td>
</tr>
<tr>
<td>ZnO-ZnO</td>
<td>ZnO-ZnO</td>
<td>Al</td>
<td>SiO2</td>
<td>2</td>
</tr>
<tr>
<td>a-ZnO-ZnO</td>
<td>a-ZnO-ZnO</td>
<td>Al</td>
<td>SiO2</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1.3: Properties of zinc tin oxide (ZTO) and zinc indium oxide (ZIO) based thin film transistors.

- S: Source, D: Drain
- Sub: Substrate
- Mobility: 
- ref: Reference
### Table 1.3: ....continued

<table>
<thead>
<tr>
<th>Channel layer</th>
<th>S-D electrode</th>
<th>Gate electrode</th>
<th>Insulator</th>
<th>Sub</th>
<th>Mobility ( \mu_f ) ((cm^2/Vs))</th>
<th>On-Off ratio</th>
<th>Threshold voltage ( V )</th>
<th>S ( V/dec )</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO(_2)</td>
<td>ITO</td>
<td>ITO</td>
<td>ATO</td>
<td>Glass</td>
<td>( \mu_f = 0.8 ) ( \mu_f = 2 ) (dep.)</td>
<td>10(^6)</td>
<td>10</td>
<td>-</td>
<td>[115]</td>
</tr>
<tr>
<td>P doped (Zn,Mg)O</td>
<td>ITO</td>
<td>Al</td>
<td>HfO(_2)</td>
<td>Glass</td>
<td>( \mu_f = 5.32 )</td>
<td>10(^3)</td>
<td>2.8</td>
<td>-</td>
<td>[116]</td>
</tr>
<tr>
<td>Sn doped Ga(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>a-Al(_2)O(_3)</td>
<td>Al(_2)O(_3)</td>
<td>( \mu_{sat} = 0.05 )</td>
<td>-</td>
<td>-6.7</td>
<td>-</td>
<td>[117]</td>
</tr>
<tr>
<td>a-ZITO</td>
<td>Al</td>
<td>Ti - Au</td>
<td>Si(_2)O(_2)</td>
<td>Si</td>
<td>( \mu_I = 5 )</td>
<td>10(^6)</td>
<td>( V_{ON} = -4 )</td>
<td>-</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \mu_I = 19 )</td>
<td>10(^6)</td>
<td>( V_{ON} = -17 )</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

semicond: semiconducting, cond: conducting, polyim: polyimide, dep: depletion mode
Table 1.4: Properties of zinc tin oxide (ZTO) and zinc indium oxide (ZIO) based thin film transistors:
Preparation technique

<table>
<thead>
<tr>
<th>Channel deposition</th>
<th>Channel material</th>
<th>Sub/annealing temp. (°C)</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF magnetron</td>
<td>ZnO &amp; a-IZO</td>
<td></td>
<td>IZO-amorphous channel and ZnO-poly-crystalline, amorphous channel devices gave better performance than poly-crystalline channel, bottom gated, TTFT</td>
<td>[62]</td>
</tr>
<tr>
<td>sputtering</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RF-PERTE</td>
<td>InO$_2$</td>
<td>350</td>
<td>bottom gated, transparent TFT</td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td>a-CdInSbO</td>
<td></td>
<td>flexible substrate, amorphous channel, top gated, TTFT</td>
<td>[106]</td>
</tr>
<tr>
<td>Reactive evaporation</td>
<td>In$_2$O$_3$</td>
<td>200, 300</td>
<td>annealing at 200° C, annealing at 300° C resulted high leakage current, poly-crystalline channel, bottom gated TFT</td>
<td>[107]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>SnO$_2$ - ZnO</td>
<td>600</td>
<td>sequential channel layer deposition and annealing, amorphous channel, bottom gated, transparent TFT</td>
<td>[108]</td>
</tr>
<tr>
<td>PLD</td>
<td>ZTO</td>
<td></td>
<td>Oxygen plasma assisted PLD, bottom gated, transparent TFT</td>
<td>[109]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>a-ZTO</td>
<td>175, 300</td>
<td>amorphous channel, bottom gated, transparent TFT, (ZnO)$_x$(SnO$<em>2$)$</em>{1-x}$ channel with $x=1/2$ and 2/3; little variation in device performance with stoichiometry variation</td>
<td>[110]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>ZTO</td>
<td>250</td>
<td>PECVD (insulator), bottom gated TFT</td>
<td>[111]</td>
</tr>
<tr>
<td>Spin coating</td>
<td>a-ZTO</td>
<td>600</td>
<td>bottom gated TFT, high off currents of the order of $10^{-8}$ A.</td>
<td>[112]</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Channel deposition</th>
<th>Channel material</th>
<th>Sub/annealing temp. (°C)</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF magnetron sputtering</td>
<td>ZIO</td>
<td>300, 600</td>
<td>amorphous (300° C) and poly-crystalline (600° C) channel, bottom gated, TTFT</td>
<td>[113]</td>
</tr>
<tr>
<td>Spin coating</td>
<td>a-IZO</td>
<td>500</td>
<td>solution processed, bottom gated TFT</td>
<td>[114]</td>
</tr>
<tr>
<td>RF magnetron sputtering</td>
<td>SnO₂</td>
<td>600 (RTA)</td>
<td>poly-crystalline channel, bottom gated, TTFT, channel conductivity was reduced (hence enhancement mode) by reducing channel thickness to 10 - 20 nm</td>
<td>[115]</td>
</tr>
<tr>
<td>PLD</td>
<td>P doped (Zn,Mg)O</td>
<td>400, 600</td>
<td>poly-crystalline channel, top gated, TTFT</td>
<td>[116]</td>
</tr>
<tr>
<td></td>
<td>Sn doped Ga₂O₃</td>
<td>poly-crystalline channel</td>
<td></td>
<td>[117]</td>
</tr>
<tr>
<td>RF magnetron sputtering</td>
<td>a-ZITO</td>
<td>100, 300</td>
<td>amorphous channel, bottom gated TFT</td>
<td>[118]</td>
</tr>
<tr>
<td>Channel layer</td>
<td>S-D electrode</td>
<td>Gate electrode</td>
<td>Insulator</td>
<td>Sub mobility (cm²/V·s)</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------</td>
<td>----------------</td>
<td>-----------</td>
<td>------------------------</td>
</tr>
<tr>
<td>a-IGZO Ti - Au</td>
<td>Ti - Au</td>
<td>Y₂O₃ Glass</td>
<td>Mo+</td>
<td>0.2</td>
</tr>
<tr>
<td>a-IGZO Ti - Au</td>
<td>n+ -Si</td>
<td>SiO₂ Glass</td>
<td>Si</td>
<td>-</td>
</tr>
<tr>
<td>a-IGZO Ti - Pt</td>
<td>Mo</td>
<td>SiO₂</td>
<td>Si</td>
<td>1.4</td>
</tr>
<tr>
<td>a-IGZO Ti - Au</td>
<td>Ti - Au</td>
<td>Y₂O₃ Glass</td>
<td>Si</td>
<td>10⁶</td>
</tr>
<tr>
<td>a-IGZO MoW</td>
<td>MoW</td>
<td>SiNₓ Glass</td>
<td>SiNₓ</td>
<td>10⁶</td>
</tr>
<tr>
<td>a-IGZO ITO</td>
<td>ITO</td>
<td>PET</td>
<td>PET</td>
<td>10³</td>
</tr>
<tr>
<td>a-IGZO IZO</td>
<td>IZO</td>
<td>HZO Glass</td>
<td>Glass</td>
<td>10⁶</td>
</tr>
</tbody>
</table>

PET: polyethylene terephthalate, YSZ: yttria stabilized zirconia
Table 1.6: Properties of indium gallium zinc oxide (IGZO)-based thin film transistors: Preparation technique

<table>
<thead>
<tr>
<th>Channel deposition</th>
<th>Channel material</th>
<th>Sub/annealing temp. (ºC)</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF sputtering</td>
<td>a-IGZO</td>
<td>RT</td>
<td>amorphous channel, top gated TFT</td>
<td>[119]</td>
</tr>
<tr>
<td>Combinatorial sputtering</td>
<td>a-IGZO</td>
<td></td>
<td>amorphous channel, bottom gated TFT, best performance for In:Ga:Zn=37:13:50</td>
<td>[120]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>a-IGZO</td>
<td></td>
<td>shift in $V_T$ to less negative value w.r.t increase in O$_2$ pressure, amorphous channel, bottom gated TFT</td>
<td>[121]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>a-IGZO</td>
<td>RT</td>
<td>amorphous channel, top gated TFT</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td>a-IGZO</td>
<td>300</td>
<td>amorphous channel, bottom gated TFT</td>
<td>[122]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>a-IGZO</td>
<td>350</td>
<td>amorphous channel, bottom gated, In:Ga:Zn=2.2:2.2:1.</td>
<td>[123]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>a-IGZO</td>
<td></td>
<td>amorphous channel, bottom gated, mobility was increased after Ar plasma treatment</td>
<td>[124]</td>
</tr>
<tr>
<td>Co-sputtering</td>
<td>a-IGZO</td>
<td></td>
<td>PECVD at 330º C (insulator), amorphous channel, bottom gated, best composition In:Ga:Zn=0.65:0.23:0.12</td>
<td>[125]</td>
</tr>
<tr>
<td>PLD</td>
<td>a-IGZO</td>
<td>RT</td>
<td>amorphous channel, top gated, TTFT</td>
<td>[126]</td>
</tr>
<tr>
<td>PLD</td>
<td>InGaO$_3$</td>
<td>1400</td>
<td>single crystalline channel, top gated, TTFT</td>
<td>[127]</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>a-IGZO</td>
<td></td>
<td>bottom gated TTFT, saturation mobility remained almost stable while the threshold voltage showed small shift to higher positive values during 1000 hours of observation</td>
<td>[128]</td>
</tr>
</tbody>
</table>
1.10.1 Stability of oxide TFTs

Though there are many reports about AOS TFTs, studies on the TFT behaviour under bias stress is rather limited. In an application viewpoint, it is necessary to understand how these devices behave under bias stress. Prolonged application of gate bias on the TFTs can result in the deterioration of device performance. Two main mechanisms which are responsible for this instability are defect creation in the channel material and charge trapping in the gate insulator or at the insulator channel interface [129, 130]. Cross et al. [131] have studied the effect of bias stress on a ZnO channel TFT. ZnO was deposited on to a thermally oxidised p-type Si substrate by rf magnetron sputtering at room temperature. Thermally evaporated ITO was used as source and drain terminals. Application of positive and negative bias stress caused displacement of the transfer characteristics in the positive and negative directions respectively. Shift of threshold voltage indicates the charge trapping as the dominant instability mechanism. Unlike the case of a-Si:H TFTs, after both stress experiments, the device recovered their initial state after a period of relaxation of one hour. For low gate bias voltages, the subthreshold slope remained unchanged after both positive and negative stressing. However at large gate bias voltage, the subthreshold slope initially increased with time and then decreased. This is explained as some kind of defect creation/removal process taking place at high biases that becomes dominant over charge trapping.

Stability of transparent ZTO transistor was analysed by Görrn et al. [132]. ZTO channel layers were deposited on ATO/ITO coated glass substrates by oxygen plasma assisted PLD. PLD deposited ZnO:Al was used as source and drain. Stable device performance was observed for Zn:Sn atomic
ratio 36:64 in the channel. Both saturation mobility and threshold voltage was studied as a function of gate bias stress. In general, the change in mobility did not show a correlation to the threshold voltage shift. In this case, subthreshold voltage has not been shown any change with positive threshold voltage shift. Defects in the dielectric act as a charge trapping centre. However, devices with a negative threshold voltage shift have shown clear variations in subthreshold slope. This behavior has been explained due to the presence of traps in dielectric/semiconductor interface or in the semiconductor bulk material.

Suresh et al. [133] have reported the results of bias stress measurements on amorphous IGZO channel TFTs. The TFT consists of an ALD grown ATO insulator and ITO gate electrode on glass substrate. The IGZO channel and ITO source and drain were deposited by PLD at room temperature. Gate bias stress was carried out at $V_{DS} = 1$ V instead of the saturation regime where the effect of bias stress on the threshold voltage shift is small. They observed a positive shift in threshold voltage with a positive gate bias stress. This voltage instability has been attributed to the charge trapping in the channel/dielectric interface or in dielectric due to bias stressing. However, no change in subthreshold slope was observed after bias stressing, which shows that no additional defect states are created at the channel/dielectric interface after the device was stressed. It is also reported that with a negative gate bias stress, the transistor channel is depleted of electrons at the channel/dielectric interface and there was no charge trapping.

In a practical point of view, in addition to the stability under bias stress, the light sensitivity of the TFTs is of critical importance. In a-Si TFTs, they are shielded from light source. In transparent TFTs, it is not
possible to use shielding layers to reduce the light sensitivity. In display applications wavelengths below 430 nm are not relevant and can be blocked by suitable filters without compromising the overall appearance. Owing to the wide band gap of oxide semiconductors, the fundamental band to band absorption of wavelengths in the visible region can be neglected. However, the amorphous nature of the channel layer may create defects states in the band gap region and produces band tailing. Hence, even below the band gap energy, a significant contribution of defect states to the light absorption can be expected. In a study of the influence of visible light on transparent zinc tin oxide TFTs, Görrn et al. [134] found that all light induced changes are totally reversible. Due to the lower density of defects in the materials, the TFTs processed with higher substrate temperatures showed less sensitivity to the light and profound saturation behaviour in $V_T$.

Park et al. [135] have studied the effect of water adsorption on the performance of a-IGZO transistors grown by rf sputtering on SiN$_x$/glass substrates. The TFTs were dipped and kept in distilled water for 12 hours and then the electrical characteristics were measured in a vacuum chamber coupled with a semiconductor parameter analyzer. The adsorbed water molecules induced the formation of an accumulation layer of extra electron carriers. It can act as either electron donor or deep level acceptor like traps depending on the channel thickness. When the channel thickness is larger than the screening length $\lambda$ (the length over which the band bends to screen the applied gate field from the bulk of the semiconductor), the created traps did not respond to the applied gate voltage and hence thicker devices showed lesser degradation to subthreshold swing. For thinner devices (channel thickness $< \lambda$), the change in gate voltage resulted
band bending and simultaneous Fermi level shifting which led to the deteri­
oration in subthreshold swing. Further, the acceptor like trap formation pro­
motes a positive shift in $V_T$, which compensate for the negative $V_T$ shift due to the donor effect of some of the adsorbed $H_2O$ molecules. Hence thinner channel TFTs showed smaller $V_T$ shift compared to thicker channels TFTs.

The effect of long term gate bias stress on the performance of nanocryst­
alline indium oxide channel TFTs were reported by Vygranenko et al. [136]. Silicon dioxide layer, deposited on a heavily doped p-type single crystalline silicon wafers by PECVD at 200 °C, was used as the gate di­
electric. Indium oxide channel layers were deposited by reactive ion beam assisted evaporation. Mo was used as source/drain contacts and aluminium as gate electrode. Threshold voltage showed a positive shift initially, when a positive constant bias voltage is applied to the gate. After a stress time of around 3000 s, $V_T$ showed a slow decrease while the subthreshold slope did not show significant change during the course of stressing. When relaxed, TFT showed fast recovery of threshold voltage without annealing. The threshold voltage shift was ascribed to the charge trapping at the channel insulator interface and/or charge injection into silicon dioxide gate dielec­
tric. Because of the absence of covalent bonds, the defect state creation, which is responsible for instabilities in a-Si TFTs, is overruled in oxide TFTs.

Rameshan et al. [137] observed the improved performance in terms of off current and on-off current ratio on rapid thermal annealing (RTA) and subsequent $N_2O$ plasma treated ZnO TFTs. The XPS analysis of the TFT samples showed that the RTA treated ZnO surface had more oxygen vacancies as compared to as deposited samples. These oxygen vacancies
were reduced by subsequent N$_2$O plasma treatment which caused a better off current and on-off current ratio.

1.10.2 Conduction mechanism in amorphous oxide TFTs

There are limited resources which deals with the conduction mechanism in amorphous oxide channel TFTs. Chung et al. [138] investigated the current conduction mechanism in rf-sputtered a-IGZO thin films using model devices designed to mimic the carrier injection from an electrode to an a-IGZO channel in TFTs. They showed that the large contact resistance is originated from the bulk a-IGZO itself rather than from the interface between the source/drain electrodes. Interface limited mechanisms, such as thermionic emission and Fowler-Nordheim tunnelling, failed to fit the measured current-voltage curves. Instead, the conduction is governed by the space charge limited (SCL) mechanism at low electric field. At high field (> 0.1 $MV/cm$), thermionic injection of the charge carriers from the traps becomes important, leading to the enhancement of current flow by the SCL + Frenkel effect and Poole-Frenkel mechanisms.

1.10.3 Device performance parameters

Eventhough there are many possible applications to oxide TFTs, little efforts have been taken by the researchers to understand the various performance parameters. The DC and RF device performance of an IZO TFT has been reported by Wang et al. [139]. An SiN$_x$ gate insulator was deposited by PECVD. The device showed a threshold voltage of -2.5 $V$, on-off current ratio $> 10^5$, and saturation mobility $14.5$ $cm^2/Vs$. Device also showed a
unity gain cut off frequency of 180 MHz and maximum oscillation frequency of 155 MHz.

1.11 Relevance of present work

Transparent electronics is an emerging technology which are expected to find numerous applications like invisible electronic circuits, transparent displays, smart windows etc [140, 141]. The volume of work being carried out in the field of transparent electronic materials and transparent electronic devices by various research labs and industry shows the importance of this technology. As in all new technologies, a deep understanding of various parameters of these devices both in basic physics and in applied level is necessary before realising the final product. Several oxide materials and their compounds show properties suitable to transparent electronics and all such materials were not fully explored for this purpose. This work mainly concentrate to understand the optical and electrical properties of amorphous zinc tin oxide and amorphous zinc indium tin oxide thin films for TFT applications. Amorphous materials are promising in achieving better device performance on temperature sensitive substrates compared to polycrystalline materials. Most of these amorphous oxides are multi-component and as such there exists the need for an optimized chemical composition. For this we have to make individual targets with required chemical composition to use it in conventional thin film deposition techniques like PLD and sputtering. Instead, if we use separate targets for each of the cationic element and if separately control the power during the simultaneous sputtering process, then we can change the chemical composition by simply adjusting the sputtering power. This is what is done in
co-sputtering technique. Eventhough there had some reports about thin film deposition using this technique, there was no reports about the use of this technique in TFT fabrication until very recent time. Hence in this work, co-sputtering has performed as a major technique for thin film deposition and TFT fabrication. PLD were also performed as it is a relatively new technique and allows the use high oxygen pressure during deposition. This helps to control the carrier density in the channel and also favours the smooth film surface. Both these properties are crucial in TFT.

Zinc tin oxide material is interesting in the sense that it does not contain costly indium. Eventhough some works were already reported in ZTO based TFTs, there was no systematic study about ZTO thin film’s various optoelectronic properties from a TFT manufacturing perspective. Attempts have made to analyse the ZTO films prepared by PLD and co-sputtering. As more type of cations present in the film, chances are high to form an amorphous phase. Zinc indium tin oxide is studied as a multicomponent oxide material suitable for TFT fabrication.