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# Study of Morphological, Electrical and Optical behaviour of Amorphous Chalcogenide Semiconductor

*Mohsin Ganaie and Mohammad Zulfequar*

## Abstract

Amorphous chalcogenide semiconductor plays a key role in search for novel functional materials with excellent optical and electrical properties. The science of chalcogenide semiconductor (CS) show broad spectrum of soluble alloy and a wider band gap device that access the optimal energy bandgap. The electronic properties of these alloys can be tuned by controlling the proportion of (S, Se, Te). The chalcogenide semiconducting (CS) alloys are promising candidates because of low band gap (1.0–1.6 eV) and high extinction coefficient in the visible region of solar spectrum. The band structure of amorphous semiconductor governed the transport properties and evaluates various factors such as Tauc gap, defect states, mobility edges. In the extended and localized state of amorphous semiconductor an electron goes various transition, absorption/emission, transport which is due to drift and diffusion under DC electric fields. CS, including sulfides, selenides, and tellurides, have been broadly utilized in variety of energy conversion and storage devices for example, solar cells, fuel cells, light-emitting diodes, IR detector, Li/Na-ion batteries, supercapacitors, thermoelectric devices, etc. Here, we report various morphological electrical, structural, and optical properties of InSeS thin films prepared by Melt Quenching thermal evaporation technique.

**Keywords:** amorphous chalcogenide semiconductor, electrical properties, optical properties

## 1. Introduction

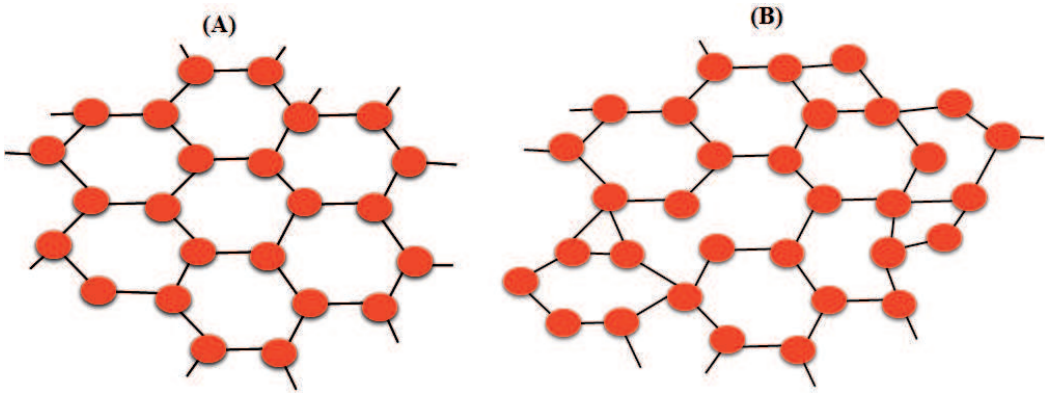
Solid can be found to prepare either in crystalline state (periodic) or in non-crystalline (disordered) state on the basis of their atomic-scale structure. The crystal has periodicity in its atomic structure and exhibit a property called long-range order or translational periodicity; positions repeat in space in a regular array to an infinite extend, as shown in **Figure 1a**. While non-crystalline state is disordered structure, does not possess long range order (or translational periodicity) as indicated in **Figure 1b** [1, 2], and also do not exhibit any discrete diffraction pattern [3, 4].

The non-crystalline solid is further divided into glassy and amorphous, which does or does not have glass transition temperature respectively [5]. The terms amorphous and non-crystalline are synonymous under this definition. The term

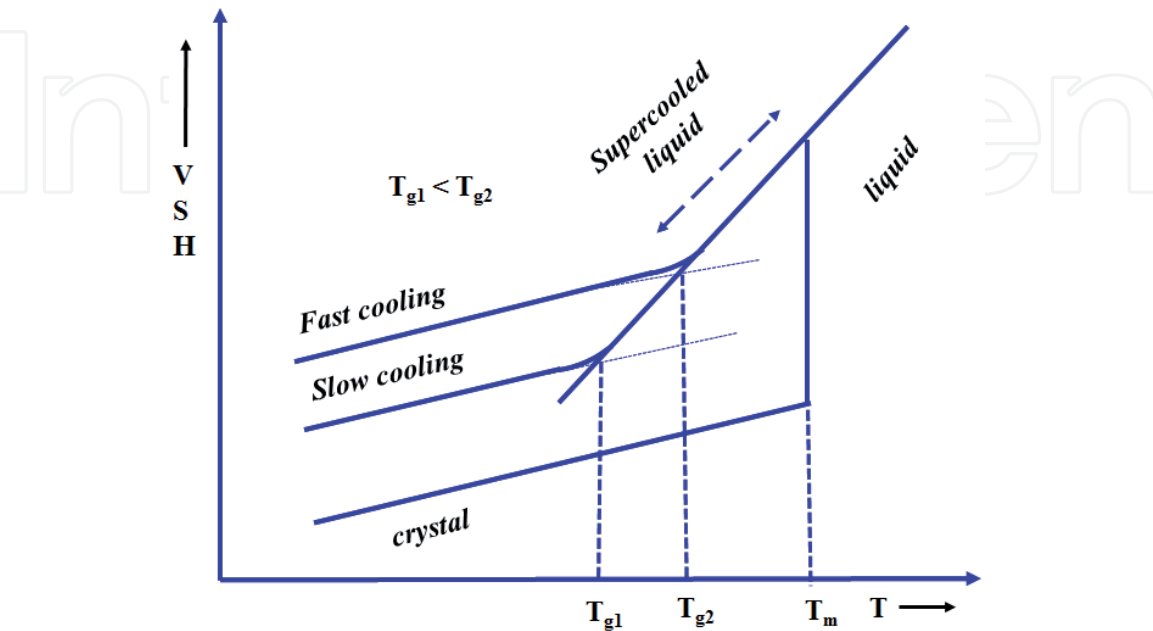
glassy have the same structural meaning; and has been reserved for amorphous solid, which have been prepared by melt-quenching and exhibits a glass transition. Whereas amorphous refer to non-crystalline material that can only be prepared in thin film form on glass substrate, which are sufficiently cool to prevent crystallization. Glassy materials are sub-set of amorphous solids; all glasses are amorphous but all amorphous are not necessarily glasses [6, 7].

Furthermore, the structure of amorphous materials is neither periodic as that in crystal nor completely random as that in gas. Short range order similar to crystalline materials exist in these disordered solids. The amorphous solid extend a vast range between completely perfect and completely random structure. An amorphous material does not take a definite phase, but is meta-stable or quasi-equilibrium.

The thermodynamic of liquid–solid transition is that when liquid is cooled, two events may occur either crystallization may take place at melting point  $T_m$  or the liquid will become supercooled for the temperature below  $T_m$ . As the temperature of supercooled is decreases the viscosity increases and ultimately reaches a value, which is typically of solid ( $\approx 10^{14.6}$  poise), at this stage liquid is said to be in glassy state. These changes can be observed by monitoring the change in its volume as a function of temperature as shown in **Figure 2**. The crystallization process is



**Figure 1.**  
*Comparison of short-range order in crystal (A) and non-crystal (B).*



**Figure 2.**  
*Schematic illustration of change in volume with temperature, effect of cooling rate on glass transition temperatures is also shown.*

manifested by an abrupt change in the thermodynamic variable at melting temperature  $T_m$ , which is discontinuous process. Whereas glass formation is characterized by a gradual break in the slope is a continuous process, and the region where this transition occur is known as glass transition temperature  $T_g$ . Other thermodynamic variables such as entropy (S) and enthalpy (H) exhibits a similar behavior with change in temperature. In the temperature interval between  $T_m$  and  $T_g$ , the liquid is referred to as the undercooled or supercooled [8]. The glass transition temperature  $T_g$  is different for different cooling rate, it is found that, slower the rate of cooling, the larger is the region for which the liquid may be supercooled. Thus, the glassy transition temperature of a particular material is not an intrinsic property, but depends on the thermal history of the materials. According to the nucleation theory, a liquid with a high viscosity between  $T_m$  and  $T_g$  typically exhibits a high glass forming ability with a low critical cooling rate for glass formation [9]. Thus, the glass formation is a matter bypass crystallization and nearly all materials can be prepared in a glassy state, if cooled fast enough [10, 11].

The electronic density of states in crystal is well defined by block wave function which extends throughout the solid; therefore the wave vector  $k$  is helpful in describing the electronic behavior and band gap in crystalline semiconductor. However, the definition of the band gap is not as straightforward for amorphous semiconductors, since there is no well-defined density of states, but there exist a continuous range of states with in the energy level. Due to the disorderness which causes the localization of electron, i.e. the wave function is confined within a small volume. Thus, the Shape of wave function of electron in crystal and non-crystal are extended and localized respectively. Consequently, their charge mobility in amorphous is smaller than that in crystal. The lattice vibration are also extended and localized in crystal and non-crystal, which give higher and lower thermal conductivities. This characteristic difference between the electronic band structure of crystalline and non-crystalline solids plays an important role in the electrical and optical properties. Also, their conductivity cannot generally be increased appreciably by the incorporation of impurities, because the impurity atom can satisfy only the valence requirement. Large fluctuations exist in the local arrangement of atoms, which can accommodate an impurity without leading to an extra electron or hole, thus exerting little effect on electrical properties. Due to disorderness in amorphous semiconductors it was believed that there is no use of these materials for technological applications [12, 13].

In 1955, Kolomiets and Gorunova from Ioffe Institute USSR [14], who discover the first semiconducting glass  $TlAsSe_2$  [15] in the system  $Tl_2Se.Sb_2Se-TlSe.AsSe_3$ . The investigation of Kolomiets, large number of chalcogenide glasses with varying Stoichiometry and composition can be synthesized. Later, in 1968, Ovshinsky and his co-workers [16] from Energy Conversion Devices discovered the memory and switching effects exhibited by some chalcogenide glasses. This shows that there is transition from crystalline phase to amorphous phase and back by switching the electric pulse, they called these materials as phase change materials. The switching effect consists of a sharp transition from high resistivity to low resistivity of the material, when an enough large electric field is applied. The observed switching process was reversible and could be repeated many times. Kolomiets and Nazarova [17] generalized that the amorphous semiconductors are always intrinsic and their conductivity cannot be affected with doping.

Ovshinsky, Fritzsche et al., and Kastner reports indicate that drastic change can be achieved in conductivity and activation energy by suitable preparation technique [18, 19]. Amorphous semiconductor can serve as stable infrared transmitting materials, which can use as optical materials for military purposes as lenses in night goggles, photovoltaic solar cells with high efficiencies [20, 21]. They have a wide range of photo-induced effects having a majority of applications. After this a new

effect has been observed such as photo doping radiometry, holography, optical memory effect having a huge potential application for imaging and electrophotography (Xerography).

More recently, the thin film form of these materials have gained much interest due to their structural, morphological and transport properties for their considerable use in various technological purposes. II–VI group semiconductor materials, plays a prominent part in the modern material science and technology and also for fabrication of large area arrays sensors, interface items, photo conductors, anti-reflector coating, IR detectors, optical fibers, etc. [22, 23]. The binary alloys of amorphous semiconductor are technologically important materials due to their direct and rather large gap [24]. These materials can be engineered for better application purpose by varying the composition parameter.

## **2. Classification and preparation of amorphous semiconductors**

Amorphous semiconductor can be classified as tetrahedral-bonded Si like a material such as amorphous hydrogenated silicon (a-Si-H) and related alloys like Si-Ge:H which is four fold coordinated and leads to the symmetrical bonding and also result in the formation of rigid structure having a wider application in thin film transistor, photovoltaic, sensors etc. The second class includes Chalcogenide glasses which have at least one chalcogenide atom, VI group of periodic table (S, Se, and Te) as their major constituent. The four-fold coordination of Si leads to the formation of highly symmetrical and rigid structures. On the other hand, twofold coordination in chalcogens is highly asymmetrical and the structure gives rise to greater degree of flexibility. Thus, the structure of chalcogenide is more complex than that of tetrahedral-bonded Si like material. Chalcogenide semiconductors consist of chain or ring like structures and have lone pair, so they are also called lone pair semiconductor. The oxygen is excluded in chalcogenide group which form a special class of material called as semiconducting oxide glasses. The present monograph is dedicated to the second group of materials, i.e., amorphous chalcogenide semiconductor. The classification of amorphous semiconductor is shown in **Table 1**.

The electronic density of states in crystal is well defined by block wave function which extends throughout the solid; therefore the wave vector  $k$  is helpful in describing the electronic behavior and band gap in crystalline semiconductor. However, the definition of the band gap is not as straightforward for amorphous semiconductors, since there is no well-defined density of states, but there exist a continuous range of states with in the energy level. Due to the disorderness which causes the localization of electron, i.e., the wave function is confined within a small volume. Thus, the shape of wave function of electron in crystal and non-crystal are extended and localized respectively. Consequently, their charge mobility in amorphous is smaller than that in crystal. The lattice vibration are also extended and localized in crystal and non-crystal, which give higher and lower thermal conductivities. This characteristic difference between the electronic band structure of crystalline and non-crystalline solids plays an important role in the electrical and optical properties. Also, their conductivity cannot generally be increased appreciably by the incorporation of impurities, because the impurity atom can satisfy only the valence requirement. Large fluctuations exist in the local arrangement of atoms, which can accommodate an impurity without leading to an extra electron or hole, thus exerting little effect on electrical properties. Due to disorderness in amorphous semiconductors it was believed that there is no use of these materials for technological applications.

Tetrahedrally bonded semiconductor		Amorphous chalcogenide semiconductor		Semiconducting oxide glasses
C	InSb	S	Cd-Se-S	V <sub>2</sub> O <sub>5</sub> -P <sub>2</sub> O <sub>5</sub>
Si	GaAs	Se	In-Se-S	MnO-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>
Ge	Si-Ge:H	Te	MWCNT/SeTe	V <sub>2</sub> O <sub>5</sub> -PbO-Fe <sub>2</sub> O <sub>3</sub>

**Table 1.**  
*Classification of amorphous semiconductor.*

Amorphous solid can prepared from all phases of matter, solid, liquid or vapor as starting materials, but the deposition from vapor or liquid phases are more considerable. Since amorphous solid are less thermodynamically stable (it possesses a greater free energy). The preparation of amorphous material can be regarded as the addition of excess of free energy. Many preparation techniques are possible, depending on what kinds of materials are required for research and/or applications. Melt quenching is one of the oldest techniques use to prepare amorphous solid especially, bulk glasses. When thin films are required different techniques are used such as, thermal evaporation, chemical vapor deposition, Gel desiccation, Electrolytic deposition, Sputtering, Chemical reaction, Reaction amorphization, Irradiation, Shock-wave transformation, Shear amorphization, Glow discharge decomposition. In this thesis, thermal evaporation technique is used for the preparation of amorphous semiconductors in thin film form under a vacuum of  $10^{-6}$  Torr.

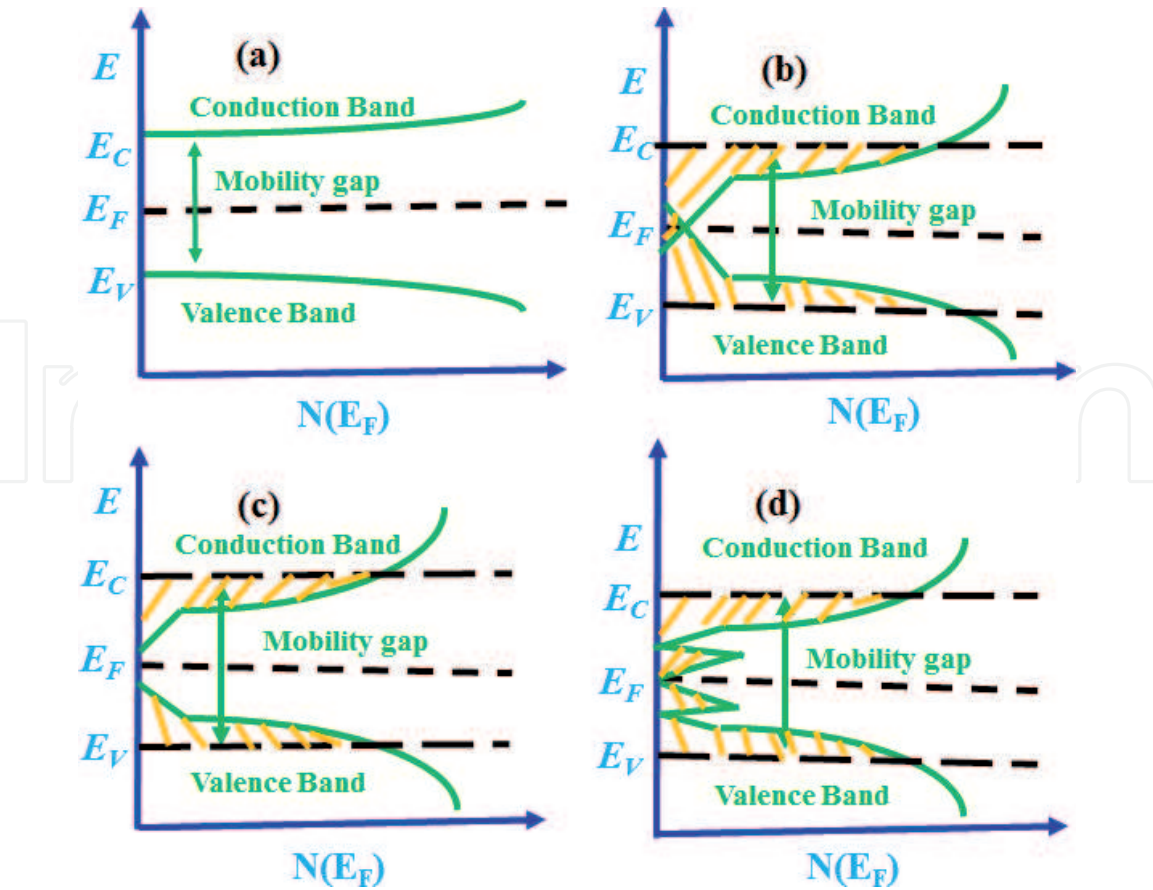
### 3. Band models of amorphous semiconductors

The significance of the band theory is used to explain or predict the properties of materials like electrical and optical. The band itself denotes the number of electronic states per unit energy per electron. In case of crystalline solid, the band diagram is represented in **Figure 3a**, which shows two results, Sharpe definite edges where the density of states decreases to zero and the wave function is extended throughout the solid. Band theory of amorphous semiconductor was first explained by Mott [25]. Based on Anderson's theory [26] sufficiently large amount of disorder results in the localization of all electronic states in the band. These localized states do not occupy all the energy states in the band, but form a tail above and below the band. The localized and delocalized regions (tail states) can be found separately by the mobility edge.

Several models have been proposed to account for the high density of defect level and also for the band structure of amorphous semiconductors, where the energy distribution and density of states (DOS) is main concerned. The existence of localized states in the tails of valence band and conduction band and of a mobility edge separating the extended states from the localized states.

#### 3.1 Cohen-Fritzsche-Ovshinsky (CFO) model

In 1969, the energy state described by Cohen, Fritzsche and Ovshinsky [27] assumed that tail states exist across the gap that separates the localized states from the extended ones. In their energy band model, the disorder is sufficiently high that causes conduction and valence band tails overlap in the mid gap leadings to appreciable density of states in the overlapping band, **Figure 3b** shows CFO model.



**Figure 3.** Schematic density of states diagrams for amorphous semiconductors. (a) Crystalline semiconductor, (b) Cohen-Fritzsche-Ovshinsky model, (c) Davis-Mott model showing a band of compensated levels near the middle of the band gap, and (d) Marshall and Owen model [19].

There is a sharp mobility edges in each band that separate the extended states from the localized states. As a result of band overlapping redistribution of electron must take place which form filled states in the conduction band tail, which are negatively charged and empty states in the valence band which are positively charged. The CFO model was especially proposed to understand the electrical switching properties in chalcogenide glasses. The primary objection to the CFO model is the high transparency observed in the chalcogenide glass, below a well-defined absorption edge.

### 3.2 Davis and Mott (DM) model

Davis and Mott [28] suggest a model for electrical conduction in amorphous solid in which tail of localized states should be narrow and should extend a few tenths of an electron volt into the forbidden gap. Defects in the random network such as dangling bonds, vacancies etc., give rise to the band compensation level near the middle of the gap. The central compensated band may be split in to a donor and acceptor band results in the pinning of Fermi level at center. It was suggested by Mott that as the transition from extended to localized states, mobility drop by several order of magnitudes producing mobility edge. **Figure 3c** shows Davis Mott model, here E<sub>C</sub> and E<sub>V</sub> represent the energies, which separate the range where the state are extended and localized. The energies at E<sub>C</sub> and E<sub>V</sub> act as pseudo gap and define as a mobility gap.

Deviation from the 8-N rule will raise the topological defects, unsatisfied, or broken, or dangling bond, these kinds of defects should presents in large quantities of amorphous network. Anderson postulated [29] that negative effective correlation

energy, or negative  $-U$ , centers in these amorphous chalcogenide semiconductors is due to the strong electron–phonon coupling.

Marshall-Owen [30] modified the Davis-Mott model suggested that the position of Fermi level is determined by well separated band of donor and acceptor level with some overlapping in the upper and lower halves of the mobility gap respectively **Figure 3d**. The self-concentration of the donor and acceptor takes places in such a way that Fermi-level remain in the mid of the gap.

### 3.3 Street and Mott model

Based on Anderson's idea, Street and Mott [31] proposed the model of charged defects states, instead of neutral dangling bonds in the band gap region around the Fermi level in amorphous chalcogenide materials. A bond is transferred from one chalcogenide atom to another resulting in two defects: one negatively charged, and other positively charged, labeled respectively ( $D^-$  and  $D^+$ ),  $D$  stand for atom having dangling bond. These ( $D^-$  and  $D^+$ ) exist in a more stable way than neutral  $D^0$ . It is proposed that the reaction is isothermal, and exothermic in nature. These charged defects states are electron-spin resonance (ESR) inactive, because all electrons are paired. This model assumes that electron–phonon interaction makes electron pairing energetically favorable at defects.



This model successfully explains variety of external induced phenomena in chalcogenide semiconductor such as photoconductivity, thermal process, luminescence etc.

### 3.4 Kastner Adler and Fritzsche (KAF) model

Later on Kastner, Adler and Fritzsche [32] proposed a model know a valence-alternation pair (VAP) for the formation of over-coordinated defects through the involvement of lone-pair electron. Amorphous chalcogenide are therefore called lone-pair (LP) semiconductors. The tetrahedrally bonded amorphous chalcogenide semiconductor only two of the three  $p$  orbitals can be utilized for bonding, which split into the bonding ( $\sigma$ ) and anti-bonding ( $\sigma^*$ ) molecular states, that are subsequently broadened into the valence and conduction bands respectively. One normally finds chalcogens in twofold coordination. This leaves one non-bonding electron pair, termed lone pair (LP), these lone-pair, electrons form a band near the original  $p$ -state energy.

Emin [33], in 1975, proposed that charge carriers in amorphous semiconductor may enter self-trapped states (small-polarons) which is due to the polarization in the surrounding lattice. Emin suggest that the presence of disorder tends to slow down the carriers, which may leads to the localization of carrier in that states. Emin explain various experimental data of amorphous semiconductors such as thermos-physics, Hall-mobility, DC conductivity in the framework of exciting polarons theories.

## 4. Preparation of amorphous semiconductors

### 4.1 Melt-quenching technique

Melt quenching is one of the oldest technique use to prepare amorphous solid especially bulk glasses, In this method a melt is rapidly cooled by simply turning

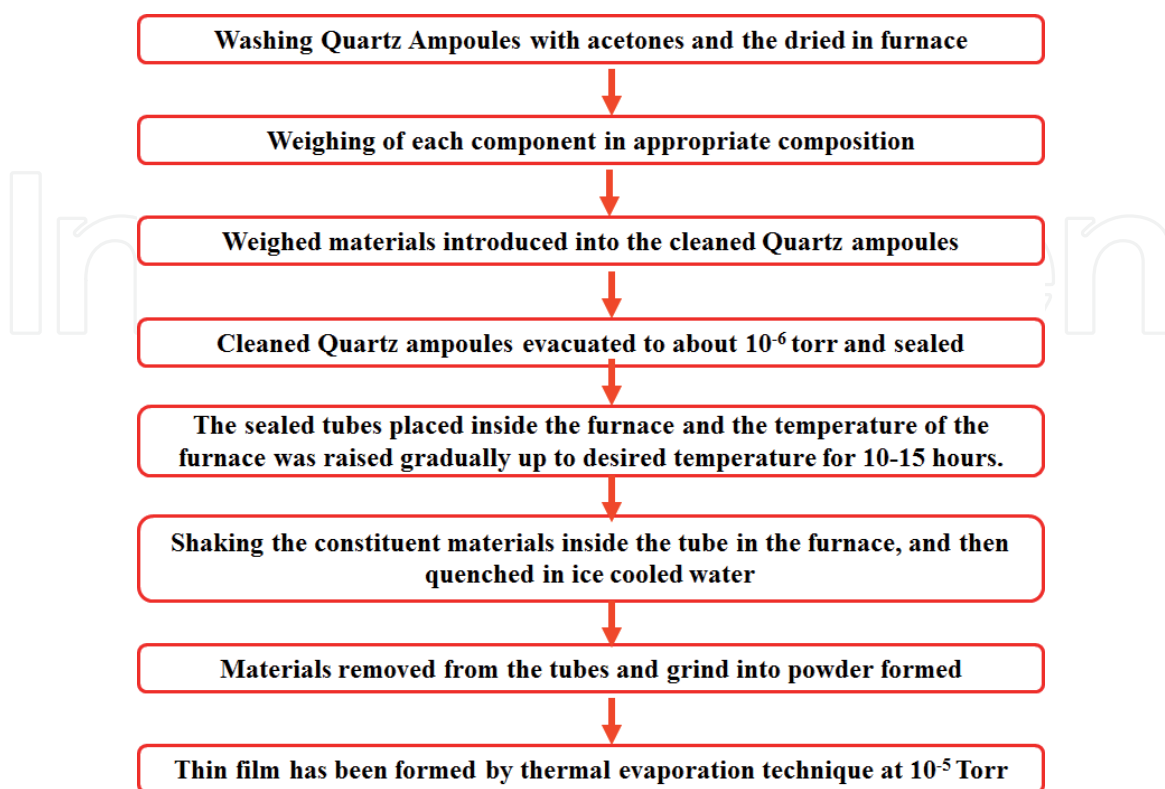
off the furnace, or rapid cooling in ice cooled water or liquid nitrogen depending upon the required cooling rate. Upon cooling a liquid below its melting point it will crystallize to form glasses. Amorphous material is formed by the process of continuous hardening (i.e., increase in viscosity) of the melt. An essential feature of glass formation from melt is fast cooling which prevent nucleation and growth [34].

The constituent elements having high purity (99.999%) with desired compositional ratio, according to their atomic mass ratio have been weight using electronic balance least count ( $10^{-4}$  gm.) were sealed in Quartz ampoules and maintaining a vacuum of order ( $10^{-6}$  Torr). The flow chart for the preparation of amorphous semiconductor is given in **Figure 4**.

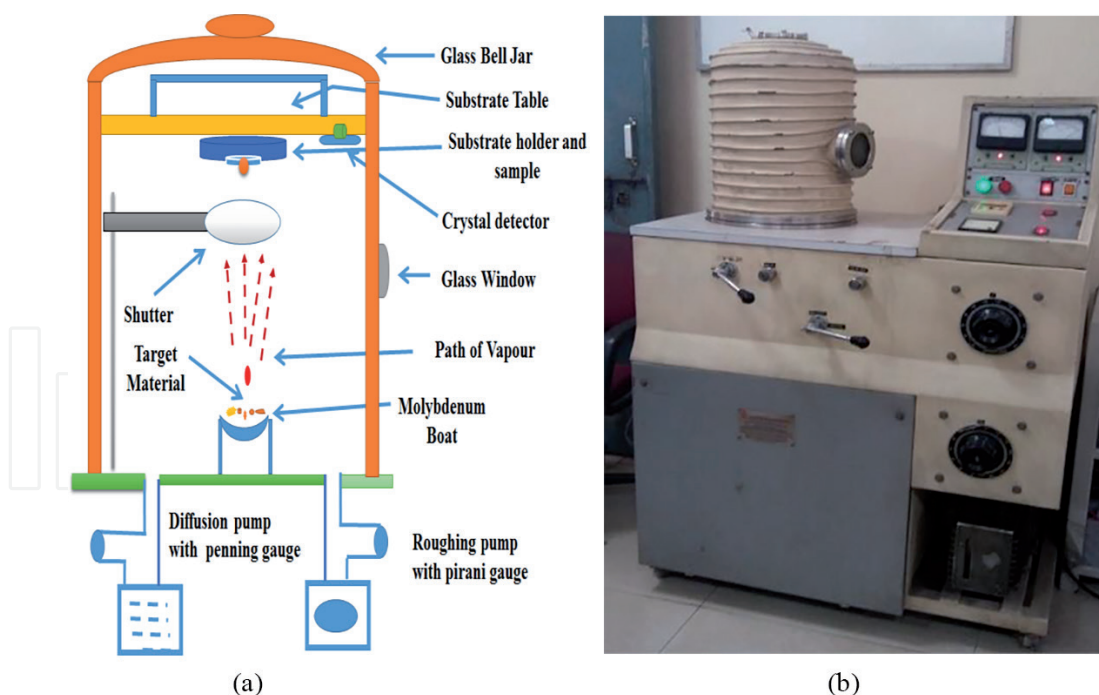
The sealed ampoules were then placed in a rocking furnace where continuous heating is done at rate of 4–5 K/min to ensure the homogenization of the melt. In case of amorphous semiconductors materials, an ice cooled water is used to produce the glassy state. The quenched samples were removed by breaking the quartz ampoules. The obtained shiny bulk samples are grinded into fine powder using pastel and mortal.

## 4.2 Thermal evaporation technique

This technique is mostly use for the preparation of materials in thin film form, in which a material to be evaporated is placed in a boat. Schematic diagram of vacuum chamber is shown in **Figure 5**. Vacuum chamber containing molybdenum boat, where the source material is placed. The boat is connected with high voltage potential difference through which boat can be heated till the material is evaporated. The material which is placed in the boat must have low melting point than the molybdenum, which can evaporate easily and uniformly spread on substrate.



**Figure 4.**  
Design flow chart for preparation of bulk amorphous samples.



**Figure 5.**  
 (a) Schematic diagram of thermal evaporation technique (b) photograph of thermal evaporation coating unit to be used.

The evaporation rate can be controlled with the help of shutter, which is located above the boat and the thickness of the deposited film can be controlled with the help of single crystal thickness monitor, which is mounted near the sample holder.

The evaporation is performed in a vacuum to avoid the contamination; chamber is evacuated by diffusion pump and backed by rotary pump. The rotary pump used to evacuate the chamber to a pressure within the operating range of a diffusion pump; this is known as rough vacuum. Once the chamber reached at the vacuum equal to  $10^{-3}$  Torr. An oil diffusion pump which can produce a vacuum of  $10^{-6}$  Torr in the chamber must be maintained for the evaporation of materials. The pirani gauge and penning gauge is used to measure the pressure. The distance between the substrate and the target materials should not be more than 15 cm. Substrate temperature is important parameter, if higher the temperature of the substrate, the material will crystallize, room temperature is quite enough for the amorphization of the materials.

## 5. Basic properties of amorphous semiconductors

### 5.1 Structural properties

Amorphous semiconductors a new discovery in 1954 by Kolomiets and Goryunova shows that these materials possess semiconducting properties, first tried group VI elements (S, Se, Te) in place of oxygen elements, which was used to prepare oxide glasses. Following the pioneering work by Ioffe and Regel [35], Ioffe realized that amorphous semiconductor attracts a lot of attention due to their unique properties. The amorphous materials could behave as semiconductor and the band gap depends on the short range order rather than long range order. Also amorphous material possesses a large number of defects, which in turn creates a large number of localized states. In crystalline materials, the band structure is completely determined by translation symmetry in its structure, since all equivalent

interatomic distance and bond angles are equal. But in amorphous material bond angle and bond lengths are nearly equal. The short order range on atomic scale is usually similar to that in corresponding crystal. Little variation in the bond length and bond angle and other imperfection results in broadening of the band edges.

There have been many discussions on the type of structure that has been developed for amorphous materials depending on their chemical nature. In order to obtain complete structure of amorphous semiconductors, following experimental tools are presented. The overall aspect of the chemical structure that constitute short range order and long range order are obtained by using X-ray, electron and neutron beams. Extended X-ray absorption fine structure (EXAFS) is a probe particularly sensitivity for investigating the local structure around the atoms. The morphology of the samples and the inhomogeneity present in the form of phase separation and voids can be examined by transmission electron microscopes (TEM) and scanning electron microscope (SEM). The Raman and infra-red spectroscopy are the mean suitable for examine the degree of disorder and chemical bonding. The medium range of amorphous network can be well understood by small angle scattering. Differential thermal analysis is used to study the variation in structures with temperature.

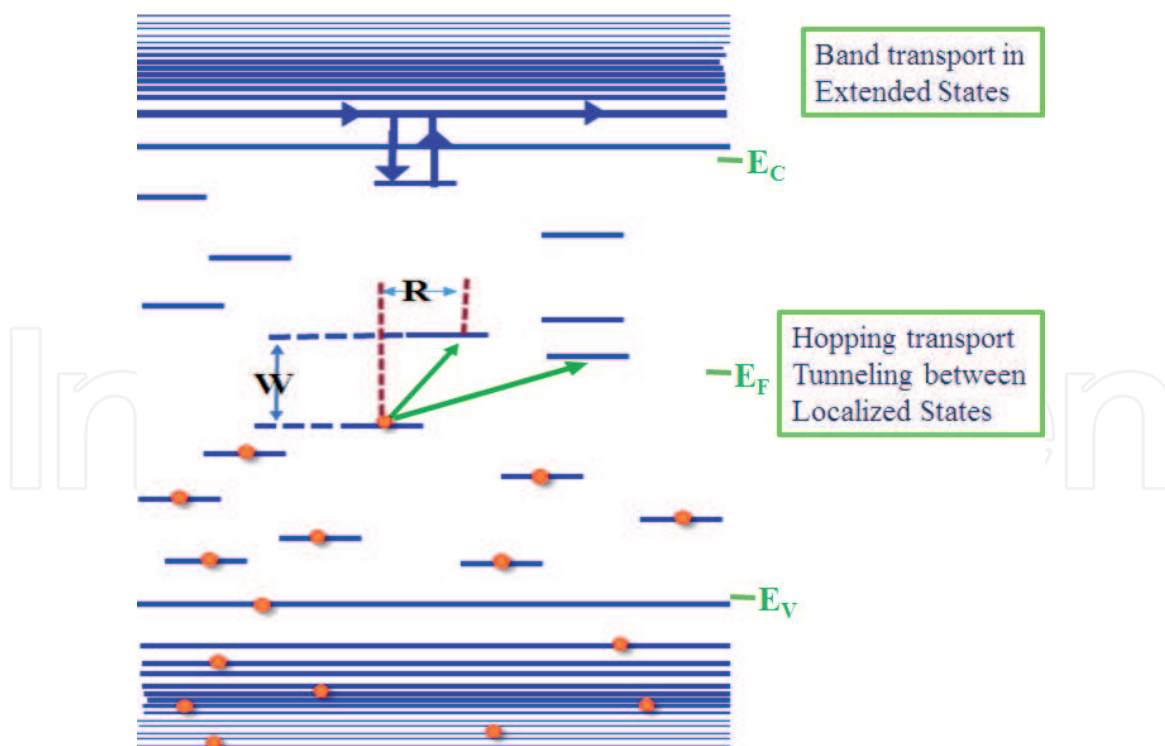
## 5.2 Electrical properties

The band states that exist near the middle of the gap arises the defects such as dangling bond, interstitial etc. These structural defects play an important role in electrical properties. Since all the electronic wave function in crystal are extended and in non-crystal the wave function of electron and hole are localized. In consequences the electron/hole mobility and the absorption in non-crystal become smaller than in corresponding crystal. Amorphous semiconductor basically has low thermal and electrical conductivity, since their band gap is large and the Fermi level lie within the gap. When talk about the electronic properties of amorphous semiconductors, the electrical conductivities at room temperature are in the range of  $10^{-2}$  to  $10^{-15} \Omega^{-1} \text{ cm}^{-1}$ . Conductivity is directly proportional to the electron/hole transport properties in the materials.

Electrical properties are primarily determined by electronic density of states, the electronic properties yielded valuable ideas like mobility edge, charge defects and activation energy. Amorphous semiconductors exhibit smaller conductivity than the corresponding crystal. Generally there are two type of conduction, band conduction (DC conduction) and hopping conduction. The band conduction occurs when the carriers would excite beyond the mobility edges into non-localized states.

The charge transport properties significantly depends on the energy spectrum  $E_v$  and  $E_c$  denote the mobility edges for the valence and conduction bands, respectively. Electronic states in the mobility gap between these energies are spatially localized. The states below  $E_v$  and above  $E_c$  can be occupied by delocalized holes and electrons respectively. The nature of charge carrier transport gets altered, when the carrier crosses the mobility edges,  $E_c$  and  $E_v$ . The transport above  $E_c$  is the band conduction type for electrons and the transport below  $E_v$  is band conduction for holes. Mostly the conductivity in amorphous semiconductor at higher temperatures is dominated by band conduction but, at lower temperatures, hopping conduction dominates over band conduction. **Figure 6** shows the different types of conduction in amorphous semiconductor.

Davis and Mott predict the DC conductivity of amorphous semiconductor, depending on the temperature range, three conduction mechanism are possible [36].



**Figure 6.**  
*Different types of conduction in amorphous semiconductor.*

### 5.3 Optical properties

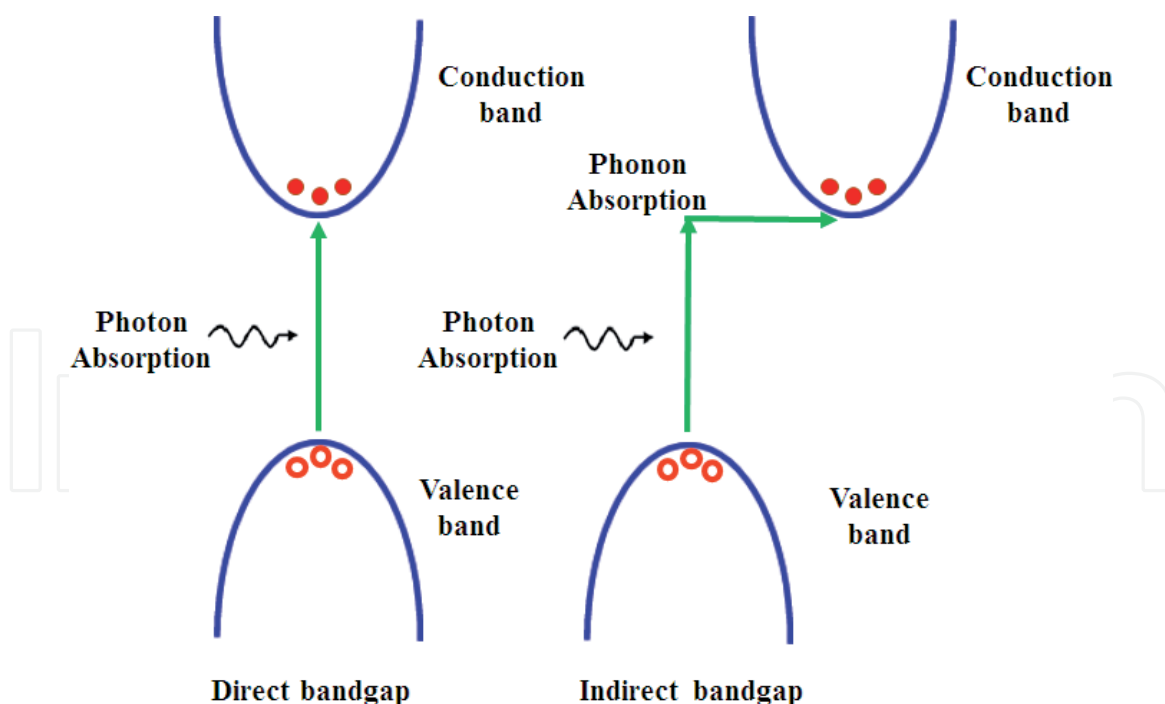
Amorphous semiconductor are the promising candidate for the photonic application owing to their interesting optical properties like high absorption coefficient, high efficiency of radiative recombination, high photosensitivity and nearly matching band gaps with visible region of solar spectrum. The design and realization of optical components based on these materials requires detailed information on their optical properties like electronic band structure, optical transition and relaxation mechanism and also a huge amount of information about their structure, opto-electronic behavior, transport of charge carriers, etc. The band gap represents the minimum energy difference between the top of valence band and the bottom of conduction band. However the minimum of the conduction band and maximum of the valence band occur at the same value of momentum, the energy difference is released as photon, this is called direct band gap semiconductor. In an indirect band gap semiconductor, the maximum energy of the valence band occurs at different value of momentum to the minimum of the conduction band energy (**Figure 7**). Both the transition direct and indirect gives rise to the frequency dependence of absorption coefficient near the absorption edge.

In amorphous semiconductors there are three distinct regions for optical absorption curve.

- a. High absorption region ( $\alpha \geq 10^4 \text{ cm}^{-1}$ ) which gives the optical band gap between the valence band and conduction band, the absorption coefficient has the following frequency dependence [37].

$$\alpha h\nu = A (h\nu - E_g)^n \quad (2)$$

where  $A$ ,  $E_g$ ,  $\nu$ ,  $h$  are constant, optical band gap, frequency of incident radiation and plank's constant respectively. The index 'n' is associated with the type of



**Figure 7.**  
Schematic representation of direct and indirect band gap.

transition, which takes the values  $n = 1/2, 2, 3$  and  $3/2$  for direct allowed, indirect allowed, indirect forbidden and direct forbidden transitions, respectively.

- b. Spectral region with  $(\alpha = 10^2 - 10^4 \text{ cm}^{-1})$  is known as Urbach's exponential tail region. In this region the optical transition takes places between localized tail states and extended tail states. The absorption coefficient can be fitted by an Urbach law.

$$(Ah\nu)^n = \alpha_0 \exp\left[\frac{h\nu}{E_u}\right] \quad (3)$$

The exponential factor  $E_u$  indicates width of band tails of the localized states and is independent of temperature. At low temperature has a value of about 0.05–0.08 eV for most of amorphous semiconductor [38].

- c. The region  $(\alpha \leq 10^2 \text{ cm}^{-1})$  involves the low energy absorption region, defects and impurities originates in this region [39].

Extensive researches on amorphous Chalcogenide semiconductors attract the attentions of researchers and engineers begins nearly at the end of 1990s, when significant change in the physical, electrical, phase, physicochemical and structural properties induced by light of appropriate energy and intensity has been investigated. The properties include photoconductivity, photovoltaic, photoluminescence, and non-linear optical phenomena that are connected with purely electronic effects.

- a. At high temperature, conduction may take place by carriers into the excited states beyond the mobility edges, electron in the conduction extended states and hole in the valence extended states. This yield an activated type temperature dependence for the conductivity of electron as [40].

$$(\sigma_{dc}) = \sigma_0 \exp\left[-\frac{E_c - E_v}{KT}\right] \quad (4)$$

where  $E_c - E_v = \Delta E$  are the activation energy, the electron at or above  $E_c$  move freely, while below it move through an activated hopping.  $\sigma_0$  is the pre-exponential factor.

- b. At intermediate temperatures, conduction occurs by thermally assisted tunneling of carriers excited into localized gap state near the mobility edges; at  $E_A$  and  $E_B$ .

The thermal assisted tunneling process means localized electron jump from site to site with the exchange of phonon, this process is called hopping conduction. If the conductivity is carried by electron then conduction will be [41]

$$(\sigma_{dc}) = \sigma_1 \exp \left[ -\frac{E - E_v - \Delta W_1}{KT} \right] \quad (5)$$

where  $\Delta W_1$  is the hopping energy in addition to the activation energy ( $E_c - E_v$ ) needed to raise the electron to the appropriate localized states at energy  $E$ . Where  $E = E_A$  and  $E_B$  is the extremity of the conduction and valence band tail.  $\sigma_1$  is expected to be less than  $\sigma_0$  by a factor of  $10^2$  to  $10^4$ .

- c. At low temperature, conduction occurs by thermally assisted tunneling of carriers between the localized states near the Fermi energy  $E_F$ .

The carriers move between the states located at  $E_F$  via phonon assisted tunneling process, which is analogous to impurity conduction observed in heavily doped and highly compensated semiconductors at low temperatures, the conductivity is given by [42]

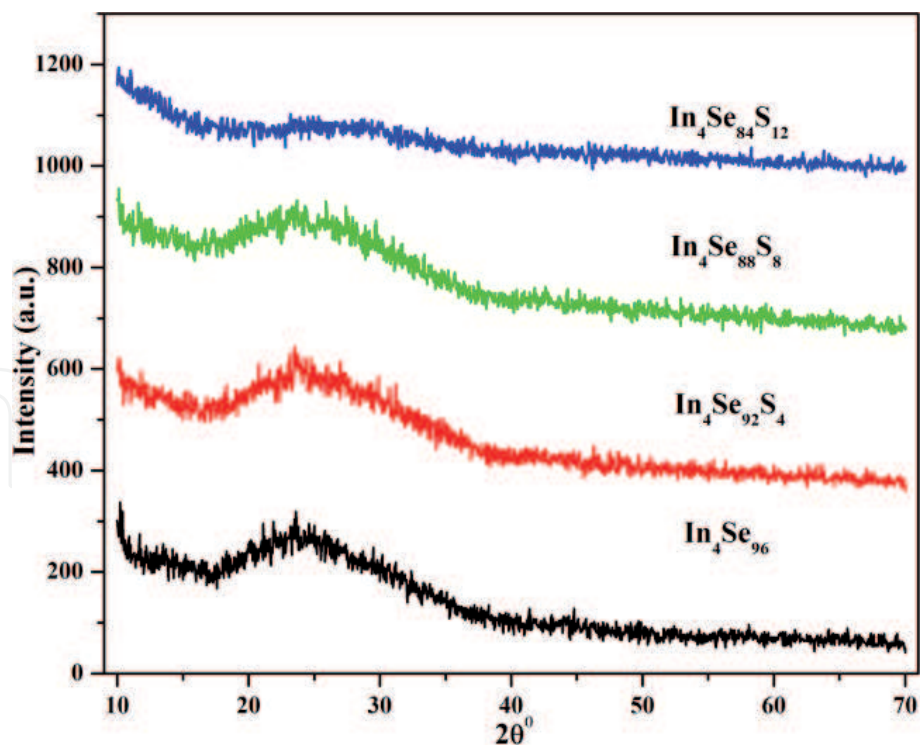
$$(\sigma_{dc}) = \sigma_2 \exp \left[ -\frac{\Delta W_2}{KT} \right] \quad (6)$$

where  $\sigma_0 < \sigma_1$ ,  $\Delta W_2$  has the same physical meaning as  $\Delta W_1$ . Since the density of states near  $E_F$  and the range of their wave-functions is probably smaller near  $E_F$  than near  $E_A$  or  $E_B$ .

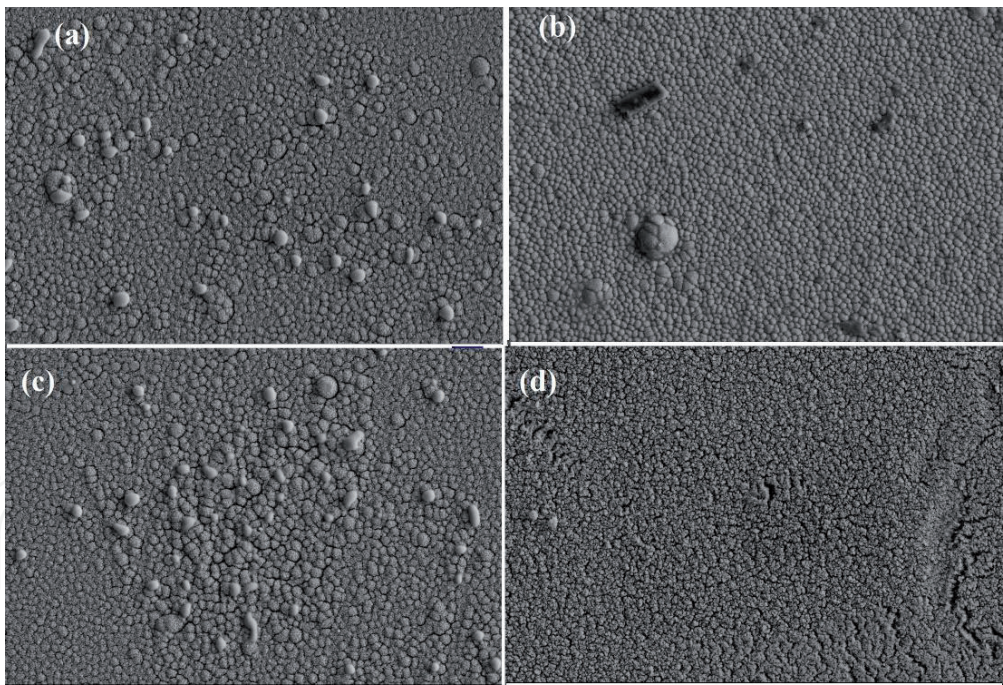
## 6. Results

Bulk ternary  $\text{In}_4\text{Se}_{96-x}\text{S}_x$  (where  $x = 0, 4, 8, 12$ ) semiconductor were prepared by melt-quenching method from high purity (99.999%) reagents. **Figure 8** show the amorphous nature of the prepared samples was carried out by a Rigaku Ultima IV X-ray diffractometer (XRD).

Morphological analysis were done by Scanning Electron Microscope (SEM), Scanning electron microscope is an influential procedure to learning the morphology, growth mechanism, particle size, shape and distribution of particles in the films. Surface morphology of thin films samples have been studied by scanning electron microscopy (FESEM) apparatus shown in **Figure 9**. We acquire SEM micrograph from Model: Sigma by Carl Zeiss employed with Gemini Column (Patented technology of Carl Zeiss) which enables intense secondary electron detection. SEM micrographs acknowledge the inclusive consistency of the thin film on glass substrate, which assert that the average grain size of the films increases from 130 to 160 nm and 190 nm with 4 and 8% of Sulfur doping, at 12% of sulfur doping it decreases to 135 nm. Thus, the improvement of development of particle size and the vanishing of small gaps between the grains after doping shows that the disorderness decreases with Sulfur concentration.



**Figure 8.**  
The X-ray diffraction pattern of  $\text{In}_4\text{Se}_{96-x}\text{S}_x$  (where  $x = 0, 4, 8, 12$ ) thin films.

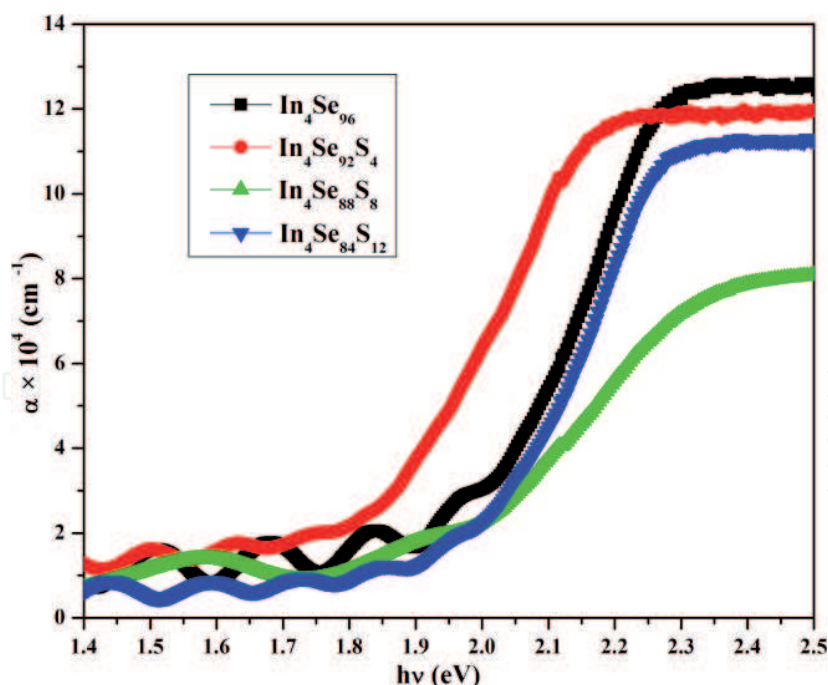


**Figure 9.**  
SEM images of (a)  $\text{In}_4\text{Se}_{96}$ , (b)  $\text{In}_4\text{Se}_{92}\text{S}_4$ , (c)  $\text{In}_4\text{Se}_{88}\text{S}_8$ , and (d)  $\text{In}_4\text{Se}_{84}\text{S}_{12}$  thin films. scale bars 200nm.

To measure the UV–Visible absorption and transmission spectra along with the energy band tail width and optical band gap in thin film of  $\text{In}_4\text{Se}_{96-x}\text{S}_x$  (where  $x = 0, 4, 8, 12$ ) has been recorded in the wavelength range of 190–1100 nm by UV–Vis spectrophotometer (Model: Comspec M550) is shown in **Figure 8**.

The relation between absorption coefficient and optical band gap is given by Tauc relation [32].

$$\alpha h\nu = A (h\nu - E_g)^n \tag{7}$$



**Figure 10.**  
Absorption coefficient ( $\alpha$ ) versus  $h\nu$  of  $\text{In}_4\text{Se}_{96-x}\text{S}_x$  (where  $x = 0, 4, 8, 12$ ) thin films.

where  $A$  is constant called the band tailing parameter,  $E_g$  is the optical band gap, which is situated between the localized states near the mobility edges,  $\nu$  is the frequency of incident radiation and  $h$  is the plank's constant. The index ' $n$ ' is associated with the type of transition. The values of absorption coefficient ( $\alpha$ ) are in the range of  $10^4 \text{ cm}^{-1}$ . With growing the sulfur concentration, the band gap is lifted to higher energy. The upsurge in optical band gap on addition of sulfur in In-Se thin films may be due to reduction in disorderness of the system and also due to decrease in density of localized states. It is well known that during the deposition of thin film, amorphous semiconductor covers large number of defects states such as dangling bond composed with some saturated bond. The addition of sulfur in In-Se system consequences the reduction of unsaturated defects making a number of saturated bonds, which is accountable for the increase in optical band gap [43] (**Figure 10**).

## 7. Conclusions

Form the above studies, one can conclude Powder sample of InSeS chalcogenide semiconductors have been successfully prepared by Melt-quenching technique and then deposited by thermal evaporation technique on ultra-clean glass substrate show smooth coverage. XRD confirm the amorphous nature of the prepared thin film. The films are highly absorptive, furthermore, the optical band gap cover the complete visible region of solar spectrum. The structural, optical and morphological studies of InSeS thin film show that it is a promising material for PV application and have the potential to be transferred in industry applications.

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