كلية العلوم
قسم الفيزياء

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كلية العلوم
قسم الفيزياء

العنوان : الموصلية الكهربية وعملية التبلور فى رقائق شبة موصلة أمورفية من السيلينيوم–انديوم

أسم الطالبة :عبير حسن محمود سراج الدين

الدرجة العلمية : ماجستير في العلوم (فيزياء)

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كليه العلوم
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رسالة ماجستير فى الفيزياء

أسم الطالبة : عبير حسن محمود سراج الدين

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Physics Department

Degree**:* ***Master of Sciences (Physics)

Title : ***Crystallization Process and Electrical Conductivity in Amorphous Selenium-Indium Semiconductor Films***

Name : ***Abeer Hassan Mahmoud Serag El-Deen***

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Abstract

Name: Abeer Hassan Mahmoud Serag El-Deen

Title: Crystallization Process and Electrical Conductivity in Amorphous Selenium-Indium Semiconductor Films

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Bulk and massive Selenium-Indium samples of the two compositions $Se_{٠,٩٥}In_{٠,٠٥}$ and $Se_{٠,٩}In_{٠,١}$ were prepared by using the conventional quenching technique after mixing the appropriate quantities of Se and In, of purity ٥N, in silica tubes sealed at $١٠^{-٥}$ Torr. The quenched ingots have been used for preparing amorphous thin films of the compositions $Se_{٠,٩٥}In_{٠,٠٥}$ and $Se_{٠,٨٢}In_{٠,١٨}$. The films were deposited on glass substrates at room-temperature using the three temperatures technique "Gürther technique".

The structural and compositional phase of the as-prepared Se-In ingots and those of the thin films have been identified using X-ray Diffraction (XRD), Energy Dispersive Analysis of X-ray (EDAX) and Differential Scanning Calorimetry (DSC).

The dc conductivity, σ_{dc}, of amorphous Se-In films was measured under vacuum in a wide range of temperature (٣١٣-٨٣k) to realize their conduction mechanism. The characteristic optical parameters (linear and non-linear) of the prepared films were determined in the spectral range ٥٠٠-٢٥٠٠ nm. Studies of non-isothermal amorphous-to-crystalline transformation on the prepared amorphous chalcogenide Se-In semiconductors performed at different heating rates (١, ٥, ١٠, ١٥ and ٢٠ deg/min) were considered and the crystallization kinetic parameters are evaluated. Also, the isothermal amorphous-to-crystalline transformation was studied for $Se_{٠,٩٥}In_{٠,٠٥}$ and $Se_{٠.٨٢}In_{٠,١٨}$ films at different isotherms lie in the range ٣٤٣-٣٩٣K. Analysis and interpretation of the obtained results are given in light of the current models and theories.

Keywords

Amorphous Semiconductors, Chalcognides, Se-In, Electrical Properties, Optical Properties, Iso-Thermal Transformations, Non-Isothermal Transformations, Crystallization Kinetics, Transport Properties, Glasses.

CHAPTER ١

THEORETICAL BACKGROUND ON AMORPHOUS SEMICONDUCTORS AND LITERATURE REVIEW ON Se-In

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Formation of amorphous phase depends on different factors such as cooling rate, viscosity of the melts, composition as well as type of bonding existing between the constituent elements of the system under consideration [٢٧]. Amorphous state becomes more probable with higher cooling rate, smaller volume of the sample and the slower rate of crystallization [٢٨].

In case of amorphous chalcogenides, chalcogens show a tendency to form chain or ring structure [٢٩]. In order to form a strong random distribution, these chains or rings must be broken down to form three dimensional network structures. This process will occur when the bond energy between other elements combined with chalcogen is much greater than those of the elemental covalent bonded solid. Thus, the proper choice of percentage of the constituent elements in the proposed system besides to the fast cooling enables to obtain the synthesized material in the amorphous state.

This chapter deals with a classification of non-crystalline bulk and thin film semiconductors, focusing on chalcogenide materials where the system Se-In is considered. Also, the electrical and optical mechanisms in amorphous semiconductors are presented. The conduction mechanism models for using the electrical conductivity as a structural sensitive property to follow the amorphous-to-crystalline transformation are also given.

١. ١. The dc Electrical Properties

In the following section, variation of the dc electrical transport in non-crystalline semiconductors will be discussed on the basis of the different proposed structural band models. To understand the structural band models, let us define first the "density of states".

١. ١. a) The Density of States (DOS)

The density of states (DOS) remains a valid concept for crystalline and non-crystalline materials and can be determined by different techniques such as field effect, capacitance measurements and photo-emission. On the other hand, mathematical methods have not yet been developed for calculating the density of states for real non-crystalline materials. Therefore, the following discussion about DOS will be based on the following assumption.

(a) The main factors determining the density of state for a given material are the first coordination number and the interatomic distance. Thus, if the formers are unchanged, no major change in DOS is likely except that due to a change in the specific volume. Coordination numbers higher than the first will, of course, influence DOS to some extent.

(b) The wave number κ is not a good quantum number for electron states in many non-crystalline materials. Either the mean free path is so short that $\Delta\kappa/\kappa$~١, or else the states are localized.

(c) In semiconductors that do not have s-like conduction and valance bands, localized states occur at the band edges E_C and E_V in the amorphous phase. These edges separate the localized states from non-localized (extended) states, and there is a drop by a factor ~ ١٠٠٠ in the shoulders. The energy difference (E_C-E_V) defines a mobility gap, E_g.

The most important feature of amorphous as compared to crystalline semiconductors is that addition of atoms with valences different from that of the host does not in general greatly affect the conductivity, i.e. they cannot easily be doped. There is evidence that structural defects play a more effective role than impurities in controlling the conductivity of amorphous semiconductors, [٣٠]. Another and equally important observation is that the activation energy for electrical conduction is approximately equal to one-half of the photon energy corresponding to the strong optical absorption. Furthermore, in cases where a comparison is possible, there is good correspondence between these energies and those occurring in an intrinsic crystalline sample of the same materials.

Although, therefore, it seems clear that the Fermi level lies near the middle of the band gap, it is uncertain whether for a given amorphous semiconductor the conductivity is intrinsic or extrinsic. By intrinsic it means that the position of the Fermi level is controlled by the densities of states in the conduction and valance bands. In such a situation, the Fermi level moves linearly with temperature in such a way as to keep the total concentration of excited electrons equal to that of holes. It should be noted, however, that even in this case, if the range of localized states at the edge of , say, the valance band (E_V) is smaller than at the conduction band edge (E_C), the number of holes excited below E_V will exceed the number of electrons excited above E_C and the materials can behave as a p-type semiconductor. While if these localized states at E_V is larger than at E_C, the material will have n-type character. In fact, most of chalcogenide semiconductors are likely to be p-type.

١. ١. b) Structural Band Models of Amorphous Semiconductors

Due to the large differences in the electronic properties of the various groups of amorphous materials, it is obvious that no single model can clarify the essential features of these materials. So, four different models have been proposed to explain the band structure of amorphous semiconductors. These models are represented in Fig. (١،١) in which the number of states per unit volume in unit energy interval, *N*(*E*), is plotted schematically against the electron energy, *E*.

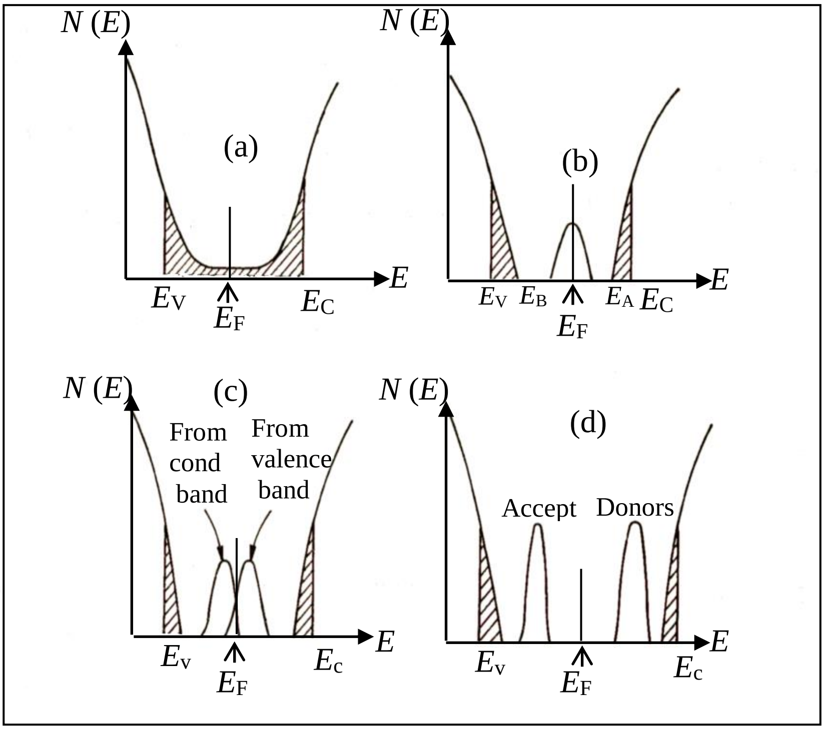

Fig. (١،١): Density of states as a function of electron energy in amorphous semiconductors; (a) CFO, (b) Mott and Davis, (c) Mott, and (d) Marshall and Owen models.

(a) Cohen, Fritzsche, and Ovshinsky (CFO) model:

This model suggested by CFO [٣١] is shown in Fig. (١،١.a). This simple band model which is based on the common feature of the covalent amorphous alloys is able to explain many of their properties. Among the novel features of this model are the overlapping of conduction and valance band tails of localized states and the sharp mobility edges. Assuming most atoms of the covalent alloys are in sites satisfying their valance requirements [٣٢]. This leads to the notion of valence band of extended states despite the randomly differing valences of the constituent atoms and to an energy separation between valance and conduction band states corresponding roughly to energy for breaking valance bonds. One therefore expects a high density of localized states tailing in the pseudo gap from the conduction and valance bands, as shown in Fig. (١،١.a). By a localized state, we mean a state with amplitude probability decreasing exponentially with distance from the centre of localization for sufficiently large distance. The fluctuations in potential on the atomic scale caused by the disorder give rise to these localized states. There are may be more than one localized state associated with a given large potential fluctuation. In general, only one of such states can be occupied at a time; double occupancy may occasionally be possible.

In this model of amorphous alloys, the tails of the valence and conduction bands overlap, which means that an electron in a given region of the material may have a higher energy than an extra electron in a nonbonding state in another part of the material. Such electrons from the top of the valence-band tail fall into spatially distinct states in the lower conduction band tail. The Fermi level E_F thus falls near the centre of the gap where the total density of states is at its minimum.

Conduction-band states are locally neutral when unoccupied, and valance-band states are locally neutral when occupied by an electron. The empty valence-band tail states therefore give rise to a random distribution of localized positive charges neutralized on the average by a corresponding distribution of an equal number of localized negative charges which are associated with the occupied conduction-band tail states. The resulting coulomb potential fluctuations of course alter the energies of states so that the occupancy of the tail states has to be considered self-consistently. These charge states above and below E_F act as efficient trapping centers for electrons and holes, respectively.

Such COF band model is probably inadequate for elemental and compound amorphous semiconductors and molecular amorphous solids with large band gaps. In the former case, there are likely to be well-defined structural defects leading to localized states of well defined energy, contradicting the supposed monotonic variation of the density of states $N(E)$ with E in the tails which leads to moving the Fermi level out of the middle of the gap. Examples for the latter case are silicon oxide and solutions of metal in liquid ammonia [٣٣] in which dissolved atoms are incorporated and greatly change the principal molecular units which make up the amorphous material and may give rise to donor or acceptor states within narrow energy regions of the gap.

This band model does not resolve the dilemma of the positive thermo-power versus the negative Hall coefficient observed in covalent alloy glasses, nor does it explain the magnitude of the density of band states near the mobility edges which is needed to explain the magnitude of the pre-exponential factor, $\sigma_{٠}$, in the conductivity formula.

(b) Mott and Davis model:

Mott and Davis [٣٠] proposes a model in which the mobility edge for electrons and holes lie between E_C and E_V, Fig. (١,١.b) a stronger distinction is made between localized states which originate from lack of long-range order and others which are due to defect in the structure. The first kind of localized states extend only to E_A and E_B in the mobility gap. The defect states from longer tails but of insufficient density to pin the Fermi level. Mott and Davis modified the CFO model by distinguishing between (i) the ranges ΔE_C, between E_C and E_A, and ΔE_V, between E_B and E_V, where the localized states lie in the bands and due to the lack of long-range order. (ii) Hypothetical 'tails' due to defects in the structure. The energies E_C and E_V separate the ranges of energy where states are localized and non-localized (extended) where the quantity $E_C - E_V$ defines a 'mobility gap'.

(c) Mott model:

In this model, the 'tails' is due to presence of defects in the structure. A dangling bond can provide a donor below the middle of the gap and an acceptor above it, but the disorder and particularly random field due to changed cavities, gives a range of energies to acquire a positive and some negative changes [٣٤]. In this sense, this model is like the CFO model where the density of state is illustrated in Fig. (١,١.c).

(d) Marshall – Owen model:

In the model of Marshall and Owen [٣٥] shown in Fig. (١,١.d), the position of the Fermi level is determined by bands of donors and acceptors in the upper and lower halves of the mobility gap, respectively. The concentrations of donors and acceptors adjust themselves by self-compensation to be nearly equal so that the Fermi level remains near the gap centre. At low temperature, it moves to one of the impurity bands