CHAPTER ONE

INTRODUCTION
AND
LITERATURE REVIEW

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A liquid can be solidified in one of two forms:

(1) A crystalline solid in which the molecules or atoms are periodically arranged on lattice points.

(2) Non crystalline solid, called amorphous, in which the molecules or atoms are characterized by the absence of periodically.

Accordingly, any solid losing the regular periodicity is known as amorphous or glass.

Information about glass structure may be provided by many techniques, including X-ray, neutron and electron diffraction, electron magnetic resonance, infrared, etc.

Generally, the non-crystalline materials may be classified into :

(1) Complete disorder materials.

(2) Metallic glasses.

(3) Chalcogenide glasses.

(4) Oxide glasses.

(5) Phosphorus glasses.

Zachariasen(1) showed that the ultimate condition for glass formation is: a substance can form extended three-dimensional networks locking periodicity with an energy content comparable with that of the corresponding crystal network. From this condition, Zachariasen(1) postulated four rules for oxide structure that allow one to choose those oxides which tend to form glasses. These rules are:

(1) The glass must contain a high proportion of cations surrounded by oxygen tetrahedra or by oxygen triangles.

(2) The number of oxygen atoms surrounding the cation must be small.

(3) The oxygen polyhedra share corners with each others not edges or surfaces and form three - dimensional networks.

(4) At least three corners in each oxygen polyhedron must be shared.

In this model, the glass network would contain large holes interstices which would easily accommodate elements that cannot enter the glass network structure.

Based on these assumptions, a glass can be visualised as a continuous random network extending in three dimensions.

According to Zachariasen(1), all oxides which participate in the glass formation are divided into three main groups:

(1) Network Formers:

These oxides can form continuous glass network by their oxygen ions. They have small coordination numbers of not more than four, e.g. B^{3+} and Si^{4+}.

(2) Network modifier:

These oxides can not form glass alone, but their cations can be accommodated in the glass matrix in interstitial positions and lead to modification of the glass matrix properties. They are comparatively large and have high coordination numbers and the mutual forces, with their adjacent oxygen, will be small, e.g. Na^{+} and Ca^{2+}.

(3) Intermediate oxides:

These oxides such as Al_2O_3 can act either as glass network formers or glass network modifiers. They have coordination numbers of four, five or six.

In phosphate glasses, which will be studied here, the basic building block is the phosphorus-oxygen tetrahedron. The phosphorus has a double bond to one of its surrounding oxygen atoms. Thus it seems likely that the structure of glassy P_2O_5 is a three - dimensional network of these phosphorus-oxygen tetrahedra, each tetrahedra being bonded to three other tetrahedra. It shows that in phosphate glasses, the most common structural units are chains or rings of PO_4 tetrahedra.

The local environments of transition metal ions in phosphate glasses have been investigated using different techniques such as nuclear magnetic resonance(2), Mossbauer absorption(3), electron spin resonance(4), optical absorption(5), etc.. The combining information from different techniques showed that Fe^{3+}- ion is predominantly octahedrally coordinated in phosphate glasses(6). In general the structural states of transition metal ions have been found to depend on the concentrations of the ions in the glasses(7).

There are many technological reasons for interest in the electrical properties of the glass. This interest has been greatly stimulated in the past several decades by discovery of semi-conducting glasses and high - speed switching effects that can be produced in some of these materials(8). Because of these recent developments, the literature on the electrical properties of glasses is expanding rapidly.

Since 1954 when the electronically conducting oxide glasses were discovered(9,10), glass formation and properties in the vanadium oxide - phosphorus oxide systems have been extensively studied(11-14). The electronic conductivity of oxide glasses containing transition metals is governed by the presence of transition metals in the glass in two different valency states.The conductivity in these glasses arises through electron transfer from a lower to a higher valency state ion. Several transition metal oxides, when heated with glass forming substances such as P_2O_5, Ge_2O form glasses on quenching from the melt. The loss of oxygen from the melt produces lower valency transition metal ions. In such transition metal oxide glasses the electrical conduction arises from the hopping of the electrons between the ions possessing different valency states. Recently, it was reported(15) that the electrical transport properties in some mixed transition metal oxide glasses are closely connected with redox shifts. It was found that the increase or decrease in the conductivity of the glasses by partial substitution of one redox pair by another will depend widely on the redox of the starting situation and on the efficiency of the dominant type of hopping process of the two redox pairs.

The electronic theories of the amorphous materials have been considered by many authors(16). In this chapter, we are going to give short accounts on some different models which have been proposed(17) for the description of the electronic states and their conduction properties as well as their switching mechanism.

I.1 Band Models:

Due to the large difference in the nature of amorphous semiconductors, it is obvious that any single model can not describe the essential features of all amorphous materials. In the following, a brief survey(16) about the most important models will be given :

I.1.1. The Simplest band model:

The simplest band structure model for amorphous semiconductor is shown in Fig.(I.1). It can be seen that the extended states (i.e. states for which the wave function extends through a region of macroscopic dimensions) can form an energy band rather similar to those for a single crystal and that the localized states occur towards the edges of the bands, extending them beyond where they would cut off in crystalline material.

The energies marked E_v and E_c correspond to the band edges of crystalline materials. The region occupied by localized states are shown shaded. The localized state can be found(18), when a dangling bond is formed, then a filled state is pulled out from the valence band and an unoccupied state is formed in the conduction band. In this sense the energy gap is closed. However, conductivity in the localized states is forbidden as the mobility corresponding to them is zero. Thus instead of an energy gap we have a mobility gap ΔE_μ as shown in Fig. (I.2).

I.1.2. Mott - CFO model:

This model, shown in Fig.(I.3), is derived from the concept of an ideal covalent random network structure. In this model, the valence and conduction bands are separated by a gap. Translational and compositional disorder are assumed to cause fluctuation of the potential of sufficient magnitude that they give rise to localized states extending from both conduction and valence bands into the gap. In this model, the valence

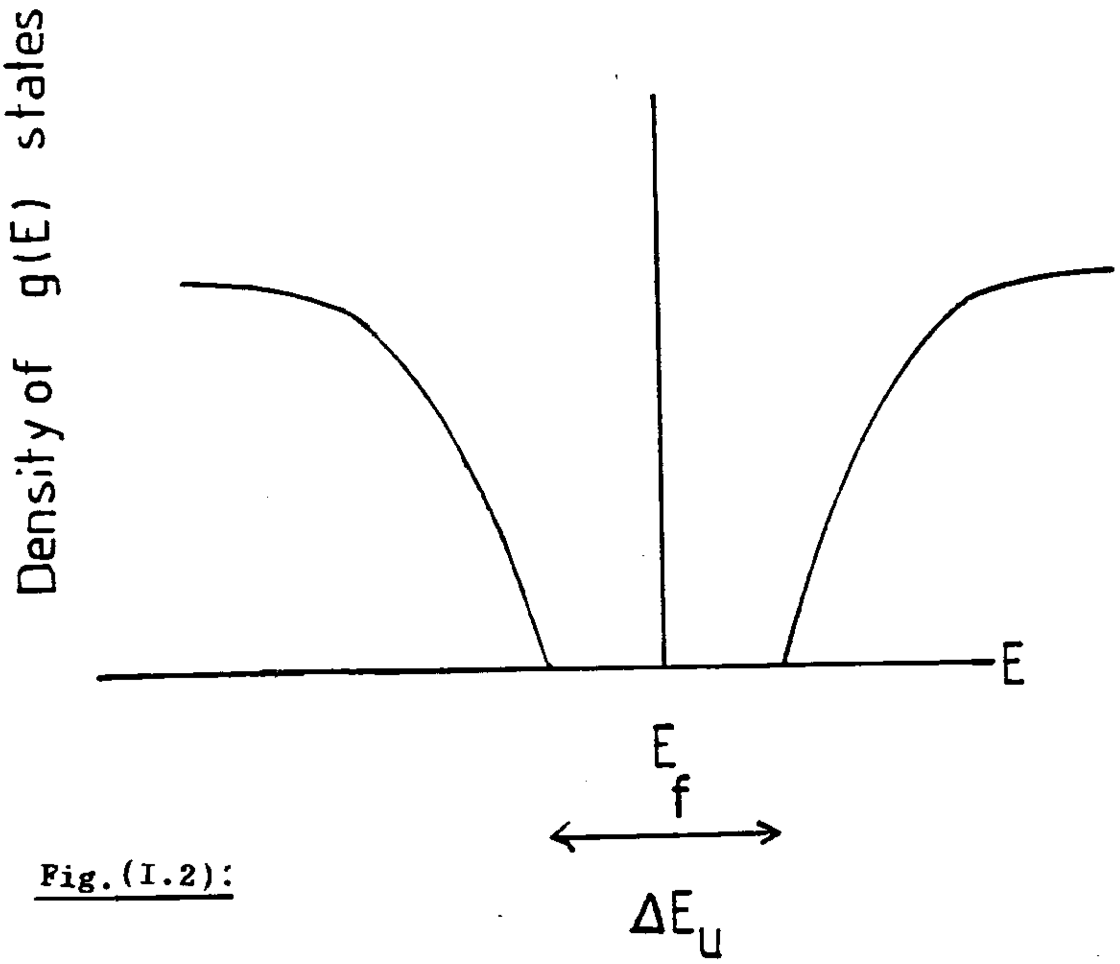

Fig.(I.2):

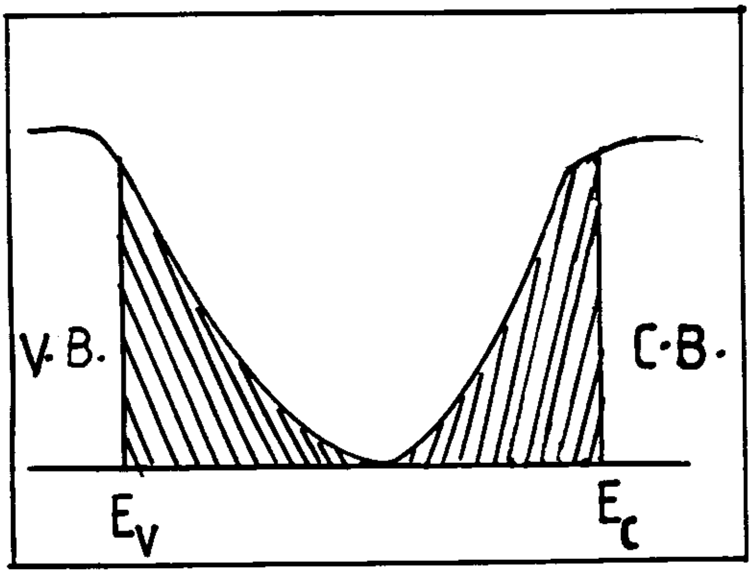

Fig. (I.1): The simplest model for amorphous semicoductors.

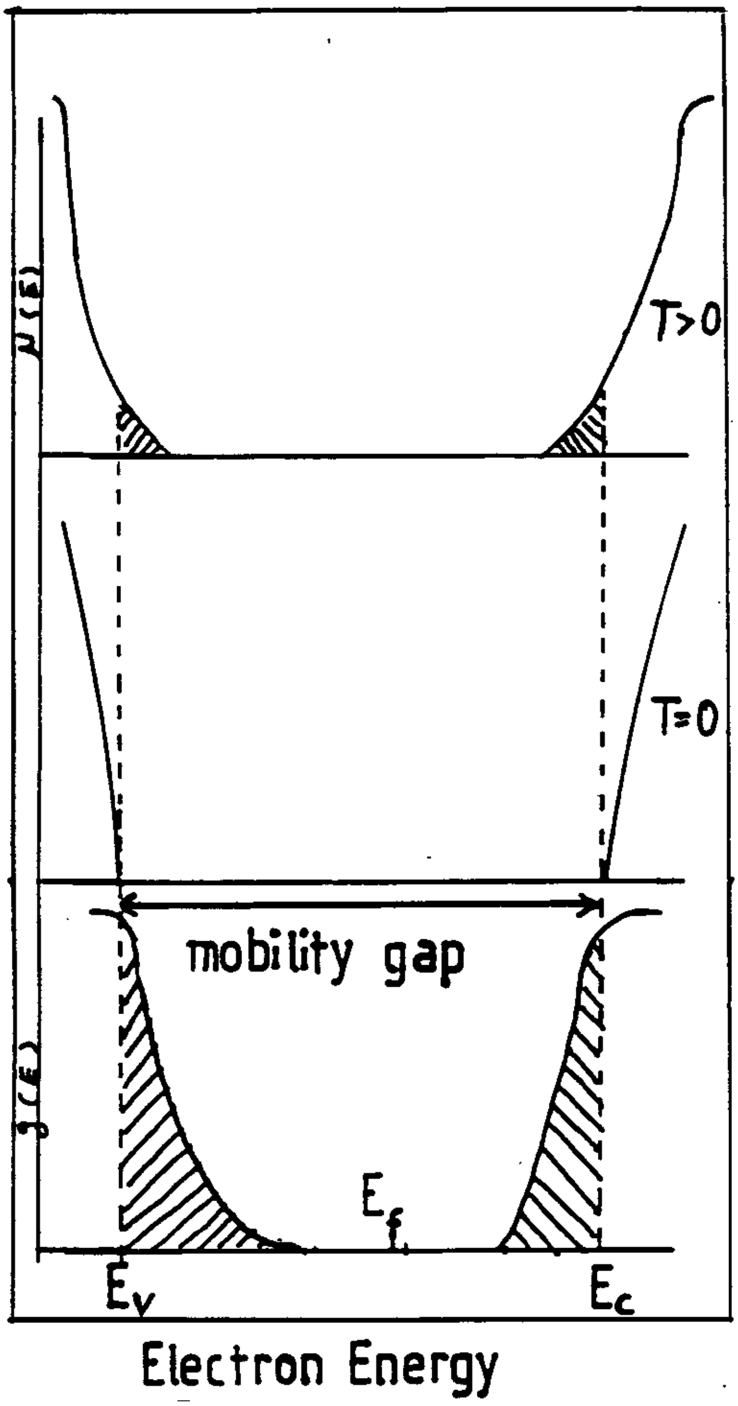

Fig. (I.3):

Sketch of Mott-CFO model for covalent semiconductors. The distribution of localized states may be non monotonic when defect states of a certain energy are prevalent.

band tail states are assumed to be neutral when occupied and the conduction band tail states are neutral when empty. Any deviations from the ideal covalent random network contribute localized states in certain energy ranges. These then give rise to a non monotonic density of localized state curve. Mott(19) found that the character of the wave function changes at critical energies E_c and E_v which saparate the extended and the localized states. Here the electron and hole mobilities drop sharply from a low mobility to a thermally activated tunneling between localized gap states. Mott(19) proposed that there exist three processes responsible for a conduction in amorphous semiconductors at different temperature ranges:

(1) At lower temperatures, conduction can occur by thermally tunneling between states at the Fermi level.

(2) At higher temperatures, charge carriers are excited into the localized states of the band tails, the conduction may occur by hopping.

(3) At still higher temperatures, carriers are excited across the mobility edges into the extended states.

The mobility in the extended states is much higher than in the localized states.

I.1.3. Davis - Mott model(20):

This band model is shown in Fig. (I.4). It is proposed that the mobility edges for electrons and holes lie at E_c and E_v. The localized state, which originate from lack of long - range order extend only to E_A and E_B. Thus the energies ΔE_c between E_c and E_A and ΔE_v between E_B and E_v, determine the position of the localized states. Whereas the defect states form longer tails but of insufficient density to pin the Fermi level.

I.1.4. Marshall-Owen Model(21):

In this model, shown in Fig.(I.5), 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.

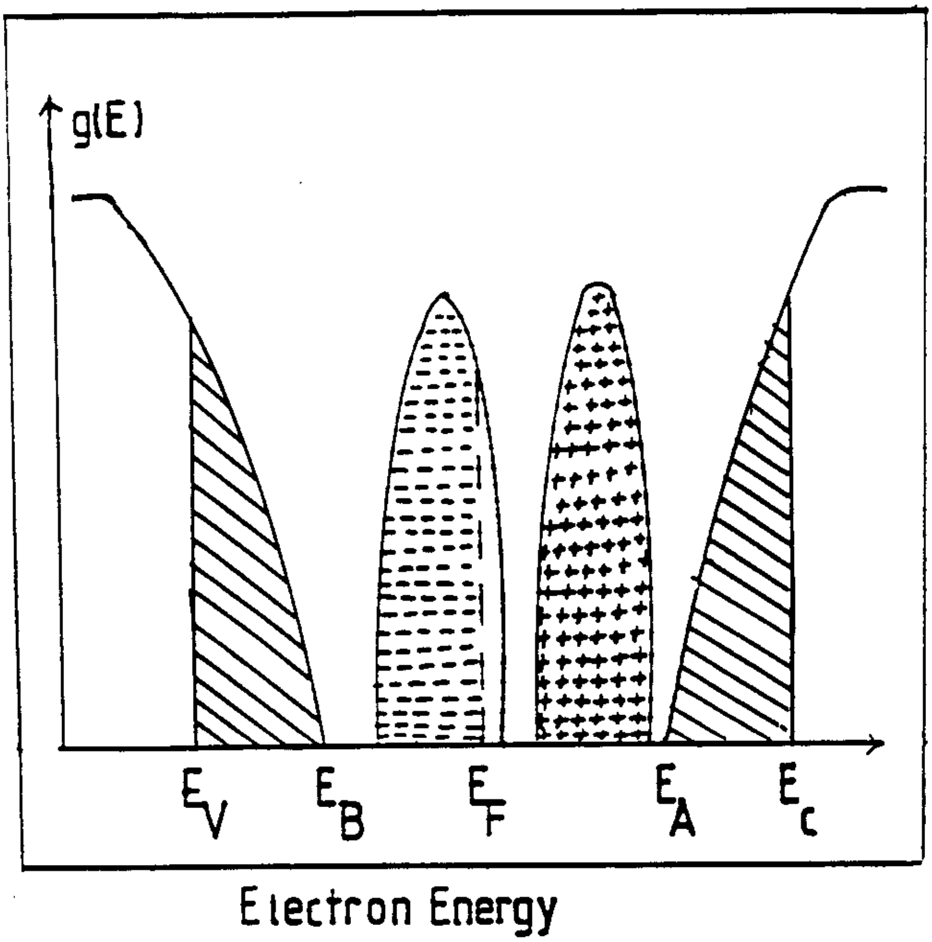

Fig.(I.5):Marshall-Owen band model.

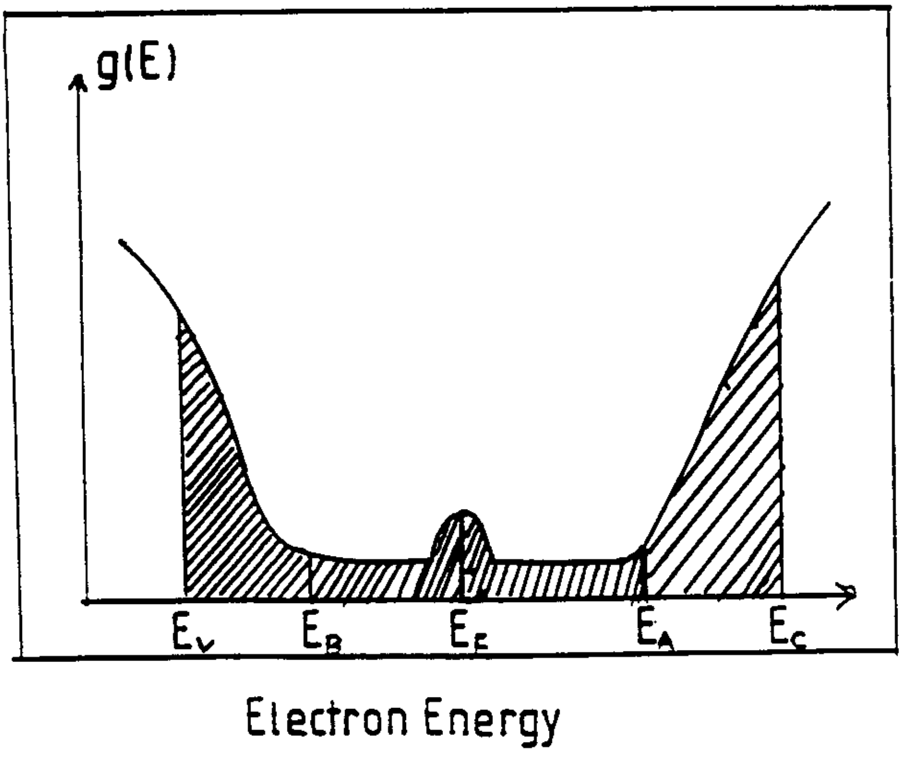

Fig. (I.4): Davis-Mott band model.

I.1.5. Sharp band edge model:

This model is useful for describing oxide glasses and semi-insulating materials(16). This model, Fig. (I.6), shows that the molecular solids and tight binding, semi - insulating materials with large band gaps have electronic structures which are relatively insensitive to disorder. In these materials tail states are negligible and a band model not significantly different from that of crystals with sharp band edges is appropriate. Since the molecular units are well defined entities, one expects that the energies of localized defect states fall into rather narrow energy ranges deep in the gap. Because the energy to create a defect state is of the order of the band gap, their number will be small and self compensation as well as dissociation of donor and acceptor type defects are energetically favored.

I.2 D.C. Electrical Conductivity of Amorphous Semiconductors:

The model described above, I.1.5, is useful to provide the density of extended and localized states g(E) and

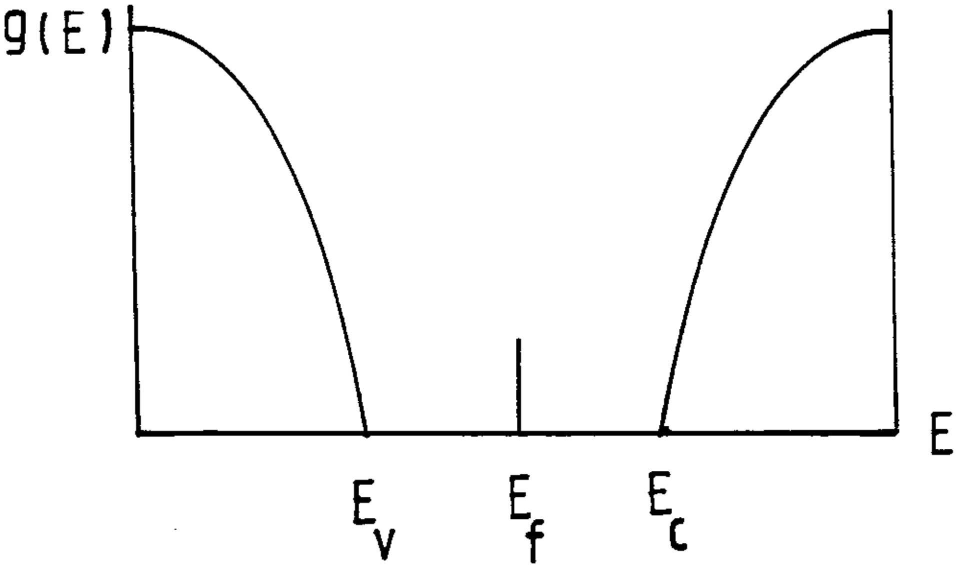

Fig.(I.6): Sharp band edge model.

the mobility $\mu(E)$ as a function of energy. So that one can calculate the dc-conductivity σ of any amorphous semiconductors using the following equation$^{(22)}$:

$$\sigma = e \int g\ (E)\ \mu(E)\ f(E)\ (1 - f(E)).dE \qquad (I.1)$$

The Fermi energy, E_f, in the distribution function, f(E), is determined by the distribution and the charge state of the gap states and the condition that the material be neutral. On applying Davis and Mott model$^{(20)}$, one distinguished three principles contributing to the conductivity:

(1) Band conduction of electrons excited above E_c

$$\sigma = \sigma_o \exp\ [-(E_c - E_f) / kT] \qquad (I.2)$$

The seperation of E_f from the mobility edge will change with T. Under the assumption that the measuring temperature range is a linear temperature dependence

$$E_c - E_f = \Delta E - \gamma T \qquad (I.3)$$

The equation (I.2) becomes:

$$\sigma = C \exp (-\Delta E / kT) \quad (I.4)$$

with

$$C = g (E_c) e kT \mu_c \exp (\gamma / k) \quad (I.5)$$

In some amorphous states it appears that μ, which corresponds to a mean free path is less than the interatomic spacing. In this case Cohen(23) suggested that the charge carriers transport proceed by means of diffusion or Brownian motion. The conductivity does not follow simple exponential law, when ΔE depends on T as a result of temperature dependent shift of E_f.

(2) Thermally assisted tunneling in the localized gap states near the mobility edges, near E_A and E_B in Fig.(I.4) or in the donor or acceptor bands of Fig.(I.5). The largest tunnel contribution arises from jumps to unoccupied levels of nearest neighbour centers. This accompanied by emission or absorption of phonon. Hence this thermally assisted tunneling process involves a hopping energy ΔW_1 in addition to the activation energy $E - E_f$ needed to raise the electron to the appropriate

localized state at E. The conductivity will thus be of the form:

$$\sigma = \sigma_1 \exp [- (E-E_f) + \Delta W_1) / k T] \qquad (I.6)$$

According to this model $\sigma_1 << \sigma_o$ and the maximum tunneling contribution shifts toward E_f as T is lowered. The conductivity curve is not expected to exhibit a constant activation energy in this range but a decreasing slope as T is lowered.

(3) Tunneling conduction near E_f

It should be of the form:

$$\sigma = \sigma_2 \exp (- \Delta W_2 / kT) \qquad (I.7)$$

where ΔW_2 is the hopping energy. 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 one expects $\sigma_2 << \sigma_1$. As the temperature is lowered the number and energy of phonons available for absorption decreases so that tunneling is restricted to seek centers which are not the nearest neighbours but which instead, lie energetically closer and within the range kT. For this so - called variable range hopping process, Mott(19) derived the relation :

$$\sigma = \text{const. } \exp\left(- T_o / T \right)^{1/4} \qquad (I.8)$$

Ambegoakar(24) found T_o as:

$$T_o = 16\,\alpha^3 / k\, g(E_f) \qquad (I.9)$$

where α , the coefficient of exponential decay of the localized state wave function.

I.3. Switching and Memory Characteristics:

In many glasses, the so called switching and memory states have been observed. This switching phenomenon, which was first reported by Ovshinsky(25), has been investigated in many ways and in different types of amorphous materials, including chalcogenide semiconductors(26), oxides(27) and organic semiconductors(28). Two kinds of processes have been found since the initial works, threshold switching and memory switching, respectively(29). In the second, the low resistance state is maintained after the current is removed, due to a crystalline filament produced by the power.

Two basic mechanisms have been proposed for the switching process : the first mechanism is based on pure electronic effects$^{(30)}$, while the second mechanism depends on thermal effects of the current flowing through the sample$^{(31)}$.

In general, the current - voltage characteristic of amorphous semiconductor, Fig.(I.7), could be divided into the following three intervals$^{(32)}$ denoting three different states:

(1) The Off - State:

In this state, the current -voltage relation shows firstly linear behaviour at low voltage (ohmic region). This region is followed by increasing the current exponential with the increase in the voltage. This behaviour is limited at certain values of voltage, current and resistance named threshold voltage " V_{th}", threshold current " I_{th}" and threshold resistance " R_{th}" respectively. The point at which the switching occured will be called the turn-over point (T.O.P.)

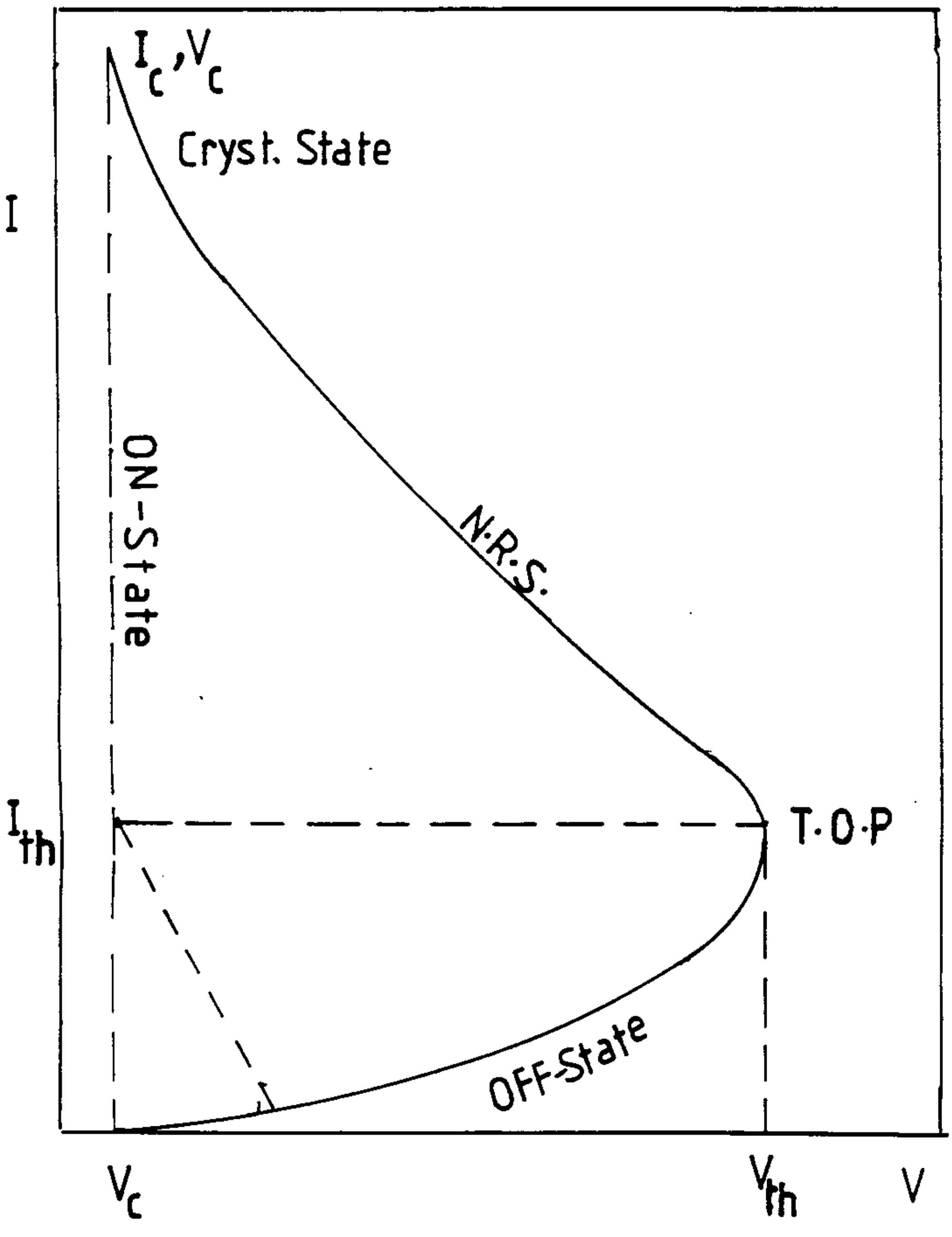

Fig.(I.7) : Typical (I-V) curve.

(2) Negative Resistance State (N.R.S):

During this state the current increases rapidly while the voltage across the sample decreases. At the end of this negative resistance state a nucleation process takes place and it ends at the beginning of the third state. A complete crystallization process occurs in the filament and the resistance of the sample becomes very low. This state is called current controlled negative resistance (C.C.N.R.).

(3) On - State:

The third state starts at the end of (C.C.N.R.) state at the point (I_c , V_c), where I_c is the crystallization current and V_c is the crystallization voltage. The material in this state is in the crystalline form, i.e. characterized by low resistance, so it is called " ON - state ".

Fritzsche(16) has been classified the switching and memory phenomena into the following five types, Fig.(I.8):

(a) The negative resistance device:

This device has an I-V characteristic which is retraceable except for some hysteresis which are observed when the current is changed too rapidly for maintaining thermal equilibrium. By using a small resistor R_L this negative resistance device can be made to switch from point (A) where the load line is tangential to the I - V curve to the point of intersection (B) of the load line and the characteristic.

(b) The negative resistance device with memory:

It has two stable states. The first state resembles that of case (a). The second is conductive. It is established at higher currents and remains without decay. The first state can be reset by increasing the current above a certain value and switching it off rapidly.

(c) Switching device:

This device has no stable operating point between the high resistance OFF state and the conductive ON state to which the device switches when the voltage exceeds the threshold voltage, V_{th}. The device switches to its original OFF state when the current is decreased below holding current I_H.

(d) The switching device with memory:

It has two stable states. The high resistance state and the mode of switching resemble device (c). The conducting ON state, which is established after switching by means of setting current, remains even if the voltage is removed entirely.

(e) The voltage controlled negative resistance with memory:

As shown in figure (I.8.e). The devices pass through a negative resistance region above a voltage V_c to a state of high resistance. The I - V characteristic is retraced when the voltage is changed slowly. However, the high resistance state is retained at low voltages when the voltage is reduced rapidly. A unique feature of these devices is their capability of existing in a large number of resistance memory states depending on the

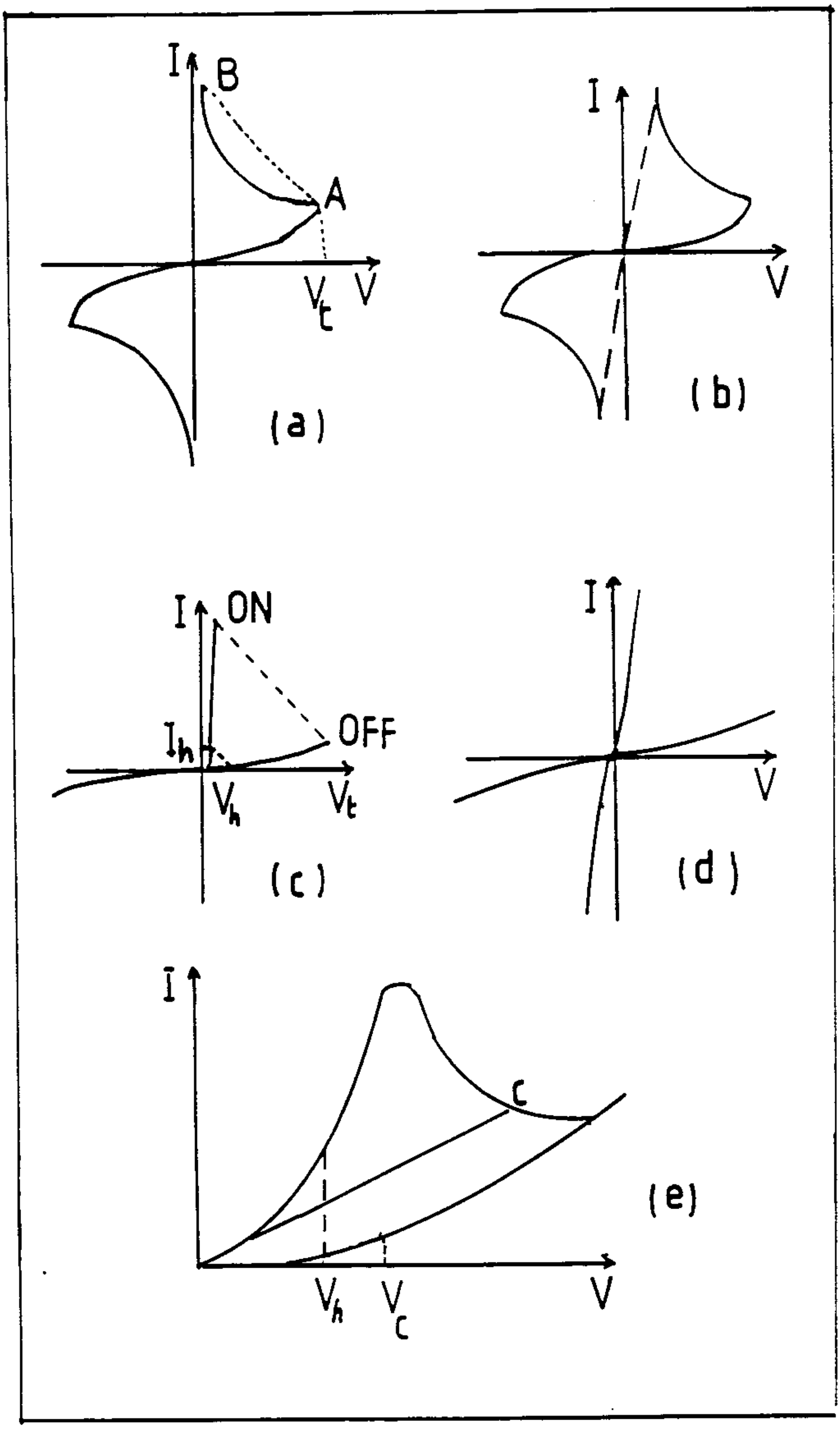

Fig.(I.8):
Classification of switching and memory characteristics;
(a) N.R.D. (b) N.R.D. with memory. (c) switching device
(d) switching device with memory(e) V.C.N.D. with memory.

choice of point C from which the voltage is rapidly reduced. These memory states are associated with electronic trapping.

I.3.1. Switching mechanisms:

The various models proposed to explain the switching process may be divided into(16):

(i) heterogeneous and (ii) homogeneous models.

In the former, a structure change occuring in the region of the current filament during switching mechanism. In the latter, the material remains homogeneous and amorphous during switching. The homogeneous model could be explained as thermal process with electronic correlations or as electronic process with thermal corrections.

I.3.1.1. Heterogeneous model:

According to this model, the first switching may alter the structure of the amorphous material in the region of the high current density filament of the ON - state in a manner such that it does not return to its original state when the device is switched off. Alloying with the electrodes and electro migration may also cause a compositional change which will get enhanced during subsequent switching events. Such forming process causes a lowering in threshold voltage and in the OFF - resistance in the device comparing with that of the virginal device.

I.3.1.2. Homogeneous models :

As mentioned before it may be divided into many theories (thermal, electrothermal and electronic).

I.3.1.2.a. Thermal theories :

The physical process in this theory is as follows : Joule self heating raises the temperature inside the semiconducting material. The resulting increase in conductivity allows more current to flow through the heated regions with the consequence of enhanced Joule heating and an increased concentration of the current flow in the heated region. A new stationary state is established when the heat conducted away from the current filament equals the Joule heat generated in that region. This is possible if the Joule heat generated reaches a plateau or begin to decrease at higher temperature.The establishing of the stationary state is a function of time. Then, the time dependent I - V characteristic is obtained as a solution, with the appropriate boundary conditions, of the heat transport equation :

$$\nabla(\lambda \nabla T)_T \; j^2 / \sigma = C_v \; dT / dt \qquad (I.10)$$

the charge conservation equation

$$\nabla J = - d \rho / dt \qquad (I.11)$$

where C_v is the heat capacity, λ heat conductivity, σ electrical conductivity.A general solution of equations (I.10 and I.11) can not be found with realistic boundary conditions. Different attempts have been made to find the realistic solution.

The work of Kroll(33) presents the most through theoretical analysis of the thermal breakdown process. The principal results of this study are:

(i) no negative resistance region and hence no switching occurs when the electrodes are perfect heat sinks;

(ii) and when effects enhancing the conductance are excluded.

In a number of studies(34,35)) the heat was assumed to flow perpendicular to the current instead of toward the electrodes. A negative resistance region is then obtained because the entire current path between the electrodes heats up in this case.

Many mathematical treatment of the thermal theories have been performed. It will be given here summary of the most important results concerning in this work.

According to Owen(36) the device current I is a function of temperature and volt

$$I = V \cdot \sigma = f(V,T) \qquad (I.12)$$

and the turn-over occurs when

$$(\partial E / \partial T)(\partial \sigma / \partial V) = 1 \qquad (I.13)$$

The turn-over temperature T' is :

$$T' = T_a + k T_a^2 / \Delta E \qquad (I.14)$$

The turnover voltage is :

$$V_{th} = 0.6\ T_a (k_b D \,/\, \Delta E \Pi a^2 \sigma_o)^{1/2} \exp\,(\Delta E \,/\, 2kT_a) \qquad (I.15)$$

Jakson and Shaw$^{(37)}$ have also presented a theoretical model for ideal thermal switching in which a sudden decrease in the resistance of the device occurs at a phase transition temperature T_t. This model suggests that the breakdown condition is reached when the temperature along the central axis of the sample becomes equal to T_t and the switching voltage is given by:

$$V_{th} = L \,/\, a\ [\ 8\ (\ T_t - T_a\ ) \,/\, \sigma_i\ ]^{1/2} \qquad (I.16)$$

where T_a is the ambient temperature, L the length, a the width of the sample and σ_i the initial conductivity of the sample. Eq. (I.16)can be expressed in the form :

$$V^2_t \,/\, R_i = A - B\, T_a \qquad (I.17)$$

where R_i is the initial resistance of the sample at the ambient temperature T_a and A , B are constants.

On the basis of the temperature - dependent conductivity of the sample in the pre - breakdown region, Duchene(38) suggested a thermal model for the switching process. According to this model V_{th} and I_{th} will thus be of the form:

$$V_{th} = [(\alpha(T_t - T_a) / \sigma_o). \exp (E_a/(k_b T_t))]^{1/2} \qquad (I.18)$$

$$I_{th} = [(\alpha(T_t-T_a) \sigma_o S^2 / D^2) . \exp (E_a/k_b T_t)]^{1/2} \qquad (I.19)$$

where α is the thermal constant, s is the cross - section of the current flow, k_b is Boltzmann constant and D is the interelectrode spacing.

I.3.1.2.b. Electrothermal theories:

Many authors(39-42) added an electronic correction terms to the thermal theories. These new theories are called now electrothermal theories. This is based on the assumption that the breakdown voltage and the ON - impedance are greatly reduced when the conductivity of the semiconductor is assumed to raise with increasing field strength, or, when space charge injection or tunneling processes are introduced to reduce the impedance of the cold layers near the electrodes. Because of the field -enhanced conductivity, the cold layer effect is diminishes in electrothermal theories and a negative resistance region can be obtained, even with perfectly heat sinking electrodes and at lower voltages(43).

The conductivity of amorphous semiconductors increases exponentially with field strength (see above). Near breakdown these field effects play a dominant rule in the conduction process, particularly at low temperatures, and therefore must be included in calculating the breakdown and current sustaining process. Due to Owen(36) an electrothermal analysis takes into account the field dependent conductivity of the active material.
The following equations have been obtained :

$$T' = T_t = T_a + (T_a^2 k / \Delta E) \qquad (I.20)$$

and the turnover voltage:

$$V_{th} = (2d\ f\ k\ T_a)/(e(a_o - dT_a))[(\Delta E/2kT_a) + \log (0.6\ T_a/V_{th}] \cdot [kdf / (\Delta E\ \sigma_o \pi a^2)]^{1/2} [1 - (V_t e a_o)/2d_f \Delta E\ ]^{-1} \qquad (I.21)$$

Sheng(44) have derived an expression for the threshold voltage V_{th} [or the threshold field E_{th}] for the ON-State of switching based on the field dependence of the conductivity.The equations obtained are:

$$V_{th}\exp(V_{th}/2V_o)=(8\lambda k_b/\sigma_o\Delta E_\sigma)^{1/2}\ T\ \exp(\Delta E_\sigma/2kT) \qquad (I.22)$$

and

$$E_{th}\exp(E_{th}/2E_o)=(8\lambda k_b/\sigma_o\Delta E_\sigma)^{1/2}(T/d)\exp(\Delta E_\sigma/2kT) \qquad (I.23)$$

where λ is the thermal conductivity of the specimen, k_b is the Boltzmann constant, T_a is the ambient temperature, d is the specimen thickness, E_σ is the conductivity activation energy in the ohmic region, V is the applied voltage and σ_o , V_o, E_o are constants. In general the temperature dependence of V_o and E_o is not known(45).

I.3.1.2.c. Electronic theories:

Discussion of different mechanisms showed that (16) the gross features of the I - V characteristic are not sufficiently unique to serve as a criterion for one or the other mechanism.

or by injection from the electrodes.

(ii) These excess concentrations in the bulk can be sustained after switching by high field regions near the contacts.

These excess concentrations, which cause the bulk to be highly conducting (but neutral), can be described by quasi- Fermi levels for electrons and holes, which split apart from the equilibrium Fermi level. The equilibrium time τ_o for the two quasi-Fermi levels to return to the equilibrium level after removal of the voltage is assumed to be long, Fig. (I.9).

I.4. Thermal Studies:

Thermal analysis is a name applied to a group of techniques having a common operating principle depending on heating or cooling the sample under investigation according to a predetermined program. So some physical property of the sample is recorded as a function of temperature on a thermal analysis curve(46). The main purpose of making thermal analysis measurements on

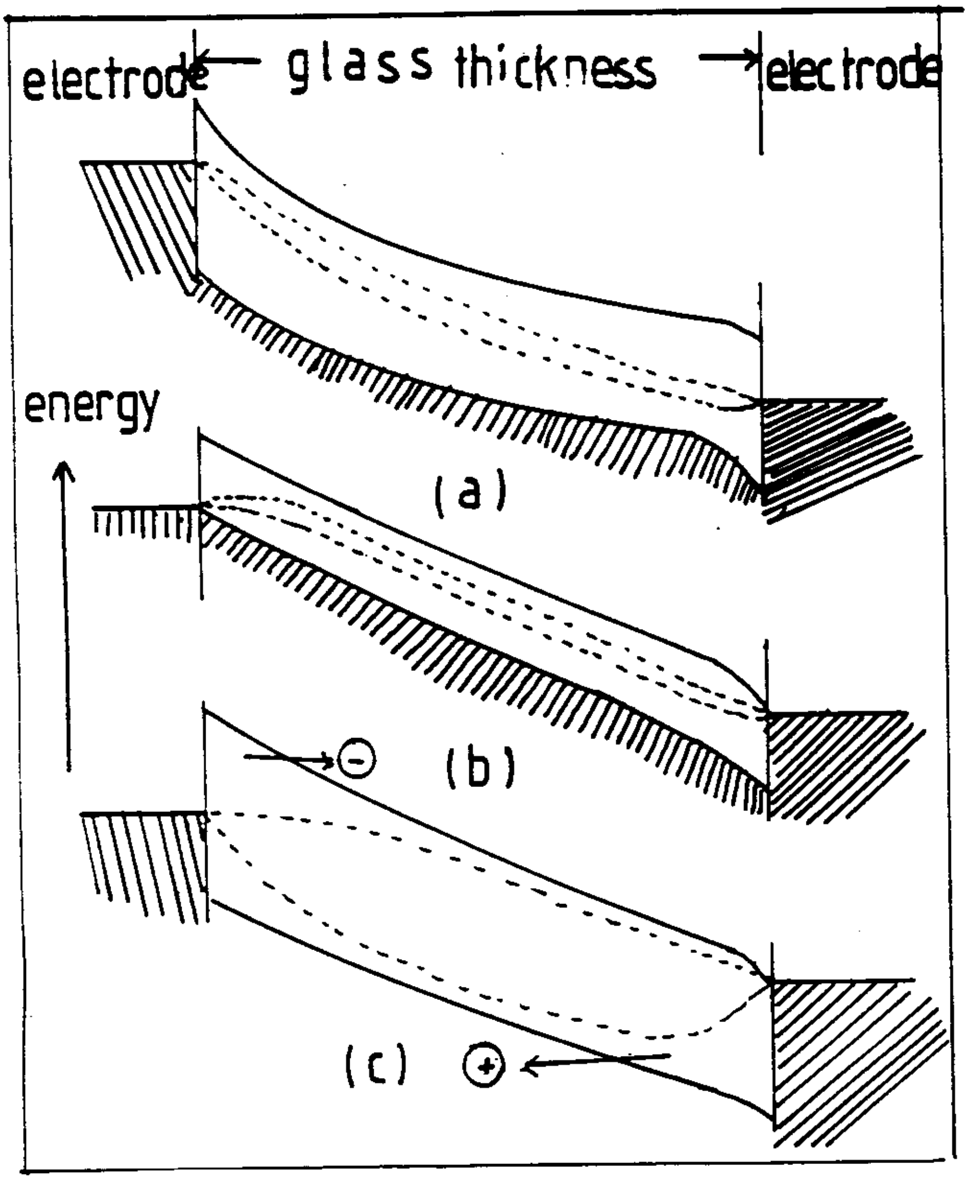

Fig. (I.9): Sketch of potential profile:
(a,b) Before switching representing two different applied fields
(c) potential profile of the ON-state after switching. Dashed lines represent the quasi fermi levels for electrons and holes. The arrows indicate injections.

glasses is seldom merely the evaluation of the measured property itself as a function of temperature, but rather the use of the thermal analysis curve to study both physical and chemical changes occuring in the sample on heating. The interpretation of a thermal analysis curve therefore consists in relating the features of the property - temperature curve to possible thermal events in the sample, i.e. chemical reactions, dissociation or physical transitions (e.g. glass transition, crystallization, etc.).

I.5. Infrared Studies in Glass:

In any molecule, not at absolute zero, the atoms are constantly oscillating about their respective equilibrium positions with the frequencies corresponding to the infra-red portion of the spectrum. If, during these oscillations, a change in the dipole moment of the molecules occurs, a periodically changing electrical field will be produced around the molecule. As a result, the emission or the absorption of radiant energy at the oscillating or the vibrating frequencies will occur. If the vibrations of a polyatomic molecule are strictly harmonic and the displacement of the dipole moment depends, in a strictly linear manner, on the atomic displacements then the normal vibrations and the change of the dipole moment produced by the normal vibrations will be dependent on each other. The result is that the vibrational spectrum will contain not only frequencies corresponding to the fundamental vibrations of the entire molecule but also frquencies associated with the vibrations of the substituent groups of the molecule. In the ideal case, the frquencies will be independent of each other, however the mechanical or electrical anharmonicity is usually present, and overtones results. Moreover, the sums or differences of the fundamentals or overtones may appear. These are called combination frequencies.

Glasses which contain atomic groups of one particular type will give transmission curves which show characteristic absorption bands for these groups. So absorption bands which are found in the transmission curves of a series of glasses may thus be attributed to the constituent which is common to all glasses. The frequencies of the vibrations will depend on the bond strength between the atoms, but may be modified to a greater or to a lesser extent by forces exerted by neighbouring atoms adjacent to the groups, giving rise to corresponding changes in the positions of the absorption bands. The groups present in glass may contain four or more atoms or ions, and so can give rise to a large number of different fundamental vibrations, the actual number is dependent on the symmetry and the nature of the groups.

So, the infra-red investigation depends essentially on associating a particular band position with a characteristic group or structural unit in a compound and noting also the maximum intensities of the corresponding absorption band. Therefore, any change occurs around the symmetry of the vibrating group due to the change in the crystal structure or due to the presence of defects will lead to a change in the vibration position of the vibrated group. Therefore, the vibrational spectra may give information about the position and valency of the ions in the glass.

I.6. Electron Spin Resonance Studies:

Electron spin resonance considers as one of the most important spectroscopic techniques which may be used to study species having one or more unpaird electrons.

The condition to be satisfied in order to observe the ESR absorption signal is :

$$\Delta E = h \nu = g\ m_{\beta}\ \beta$$

β is the magnetic induction, g is a dimension less proportionality constant called g - factor or spectroscopic splitting factor, m_{β} is the Bohr magneton ($m_{\beta} = eh / 4\pi m_e$), where e and m_e are the charge and the mass of the electron respectively and h is Planck's constant.

I.7. Crystallization of Glass:

Crystallization of glass is the process by which the regular lattice of the crystal is generated from the less ordered liquid or glassy states(47). It is generally considered as consisting of, more or less, two independent processes:

(1) Nucleation or formation of crystal centers, and

(2) Crystal growth on the formed centers(48).

(1) NUCLEATION:

For crystallization to begin, crystal nuclei must be present. Nucleation involves the initiation of regions of longer range atomic order, known as embroys, than are normally present in the molten state or in the supercooled liquids(16). When these embroys attain a critical minimum size capable of developing spontaneously into gross particles of the stable phase they are known as nuclei.

However, despite considerable research, the mechanisms by which nucleating agents induce crystallization are not yet completely clear.

(2) CRYSTAL GROWTH:

After nucleation, the nucleated glass must be heated to higher temperatures for crystal growth to proceed.

This step represents a complex process for a number of reasons. First of all, a number of phases may crystallize simultaneously. Commonly, the composition of the crystals differs from the composition of the original glass. This means that the composition at the crystal glass interface is continuously changing. In addition, portions of the primary crystal phase may start to transform by solid-state reaction to a new structural type(49).

Some additives can also markedly modify crystallization rates in glasses. While some may inhibit crystal growth and this effect may be specific to particular crystal surfaces, others may exert promoting effects.

I.8. Literature Review and Aim of The Work:

The amorphous semiconductor has been used in many applications in our daily life, (e.g. optical, dielectric, solar cells, etc.)(5). The glass materials have been also used in new technologies based on nuclear energy, space exploration, and solid - state electronic devices(5,16).

Recently analysis of the electrical properties of transition metal oxide glasses has received great attention. Vandate glasses were among the most studied systems from which many features of the electrical properties were understood(50-55). However, there remains some unsetted questions.

The electrical conduction of oxide glasses containing transition - metal is basically governed by the presence of the transition - metal in its two different valency state ion. Several investigations have been performed on oxide glasses containing two transition - metal(56-66). When one transition metal ion is replaced by another one, different behaviours for the change in conductivity values were observed. Some authors reported an initial decrease followed by an increase in the conductivity values(59-62), whereas others reported the reverse behaviour(64,65) for other systems (i.e. an initial increase following by a decrease in conductivity values). The increase in conductivity was attributed(50,62,63,65) to the hopping of electrons between the transition metal ions of the different elements in addition to the hopping of electrons between transition metal ions of the same element. On the other hand, the decrease in electrical conductivity was suggested as due to the decrease in the redox ratio(60) or due to the inhibition of the hopping process by the possible formation of bridge bonds composed of one ion from each of the two transition metal ions with one oxygen ligand. However, recently it was reported(66) that the increase or the decrease of conductivity by partial substitution of one redox pair by another depends widely on the redox of the starting situation and on the efficiency of the dominant type of hopping process of the two redox pairs.

The presence of V^{4+}-ion in vandate glasses was reported by many authors(55,67-71). The formation of this ion was attributed to the loss of oxygen from the melt of V_2O_5 during the glass preparation. The concentration of V^{4+}-ion depends on the glass composition and the preparation method and their thermal history(55,70,71). Generally, the vanadium phosphate glasses consider as mixed valence compounds where both V^{5+} and V^{4+} ions are present. It was reported(72-74) that the concentration of V_2O_5 in these glasses play a very important role in deciding their electronic properties.

Transition metal oxide glasses consider as the most important glass systems, which exhibit a rich variety of different I - V characteristics, especially both current controlled and voltage controlled negative resistance(16). Electrical switching characteristics of transition metal phosphate glasses have been investigated by a number of authors(75-78). They have suggested that the switching is attributed to a thermal origin with a formation of conduction channel in the glass. On the other hand, Monsingh(79) suggested that the electrical switching occuring in vanadium - tellurite glasses as due to electronic model and the thermal effect dominates once the electronic channel be formed in the sample.This system showed a memory behaviour and the formation of crystalline V_2O_5 in the conduction path.

The present study was carried out to throw more light on the structural, thermal and electronic properties of vanadium - phosphate glasses. The effects of composition, doping and annealing on the physical properties of the glasses have been also investigated.