CHAPTER I

There had been enormous growth in the literature on the semiconducting properties of inorganic solids, while the research in organic semi-insulating materials has been limited only at the basic level. The reason for this is that, for long, the organic molecular solids have been viewed upon as insulators. Much interest in this field has been generated from the reports that some of them also exhibit the electrical conductivity of the order of inorganic semiconducting materials.

An organic semiconductor may be defined as any compound which possesses a high degree of intermolecular carbon-carbon bonding and which it is capable of supporting some degree of electronic conduction. Jorden in 1938 and Szent-Gyorgyi in 1941 suggested that proteins may possess semiconducting properties. The earliest experimental work in the field of organic semiconductors has been done on phthalocyanines. Anthracene commands the same place among the organic semiconductors as do Germanium and Silicon among inorganic semiconductors, and is the most extensively studied substance. Its photo conductivity and dark conductivity can be used as the introduction to the experimental results for other substances. The present state of knowledge of organic semiconductors may be equated to the knowledge about Germanium
and Silicon in 1930. Therefore some theoretical and experimental work is needed before a clear picture of their electrical and photo dielectric properties emerges and their potential applications in solid state devices are exploited. There does not exist well established theoretical explanation for electrical conduction in organic solids. The same is true with the Persistent Internal Polarization in them.

A brief review of various reports available in the literature on electrical conduction, dielectric behaviour and thermo electret and photoelectret effects on organic semiconductor is presented in support of what has been said above.

1.1 THERMO AND PHOTO-ELECTRET STATE (Persistent Polarization state)

The term electret was first coined by Oliver Heaviside¹ to describe a permanently polarized dielectric. The first experimental observation and investigation of such dielectric behaviour was carried out by Eguchi using a mixture of carnauba wax, bees wax and rosin. A sample of this mixture, when heated to a higher temperature and cooled to the room temperature in the presence of a D.C. electrical stress, developed positive and negative charges on its opposite surfaces. Eguchi's electrets being prepared by simultaneous application of electric field and thermal energy to a dielectric, were later known as the ' thermoelectrets '.

¹. Oliver Heaviside (1850-1925) was a British electrical engineer, physicist and mathematician, known for his contributions to the field of electrical engineering, particularly in the areas of electromagnetic theory and the development of radio communication systems.
Measurements by Thiessen et al. 3, Wild and Stranathan 4 and Gross 5 confirmed Eguchi's finding and prove the existence of true volume polarization for the electret.

A Bulgarian scientist Nadzakov 6 discovered the polarization in sulphur by illuminating under high electric stress. The photoconducting dielectric exhibiting this phenomenon were named as 'Photoelectret'. Similarly other electret types namely (i) Radioelectret 7 (ii)Thermophotoelectret 8 (iii) Cathodo-electret 9 and (iv) Magneto-electret 10 etc. referred to in literature are significant of the physical agency used to induce polarization in the dielectric.

The application of electrets have been suggested in electrometers 11, electrostatic high voltage generators 12-14, radiation dosimeters 17-19, electret microphones 15, telephones 16, ionography 20, electrophotography 21-22, display devices 23, air filters 24 and acoustical photography 25.

1.1(a) HOMOCHARGE AND HETEROCHARGE

The polarity of the charge on electret face is described in terms of 'homocharge' or 'heterocharge' used for the first time by Gement 26. Heterocharge describes a charge with a sign opposite to that of the adjacent electrode and the charge with the same sign as that of adjacent electrode is termed a 'homocharge'. The systematic
studies of Gross\textsuperscript{27}, Baldus\textsuperscript{28}, Wikstroem\textsuperscript{29} and others\textsuperscript{30–31} have resulted in better understanding of these terms.

1.1(b) MATERIALS CAPABLE OF PERMANENT POLARIZATION

Mikola\textsuperscript{32} reported that dielectrics whose conductivity is relatively high give only heterocharge while those having low conductivity can give both homocharge and heterocharge. Mikola (Loc. cit.) and other workers, in particular Gemant (Loc. cit.) observed that polarity of a dielectric is an essential prerequisite of formation of stable thermoelectret.

Gemant (Loc. cit.) failed to prepare thermoelectrets from non-polar hydrocarbons such as paraffines. Later on Srivastava\textsuperscript{33} prepared thermoelectrets from polyethylene and Srivastava and Singh\textsuperscript{34} prepared thermoelectrets from naphthalene which is an established non-polar material.

Wieder and Kaufman\textsuperscript{35} have studied plastic electrets prepared from nylon, perspex and lucite. They observed that the initial state of surface charge was a homocharge or a heterocharge, depending on the strength of the forming field, but the final steady state charge of all these thermoelectrets was a homocharge which remained to be practically unaffected even over 60 days of storage. Johnson and Carr\textsuperscript{36} reported the preparation of a thermoelectret from molten sulfur, but it exhibited only the heterocharge. Binder\textsuperscript{37} prepared thermoelectrets made of polyvinyl chloride.
Mixture of amorphous organic and inorganic materials in the form of Indian sedling waxes have been used for the first time in this laboratory by Nath and Bhawalker\textsuperscript{38-39} and Sharma and Bhawalker\textsuperscript{40} for the preparation of thermoelectrets. Polovikov\textsuperscript{41} has reported thermoelectret state in ebonite while Wiseman and Feaster\textsuperscript{42} have studied thermoelectret state in para-methoxy diphenyl, sugar and glass. Wiseman and Linden\textsuperscript{14} succeeded in preparing thermoelectrets from pyrex glass, palmitic acid and perspex. Gubkin and Skamavi\textsuperscript{43,44} and others\textsuperscript{45} have shown that thermoelectrets could be prepared from ceramic materials like titanates of barium, calcium, strontium and other inorganic dielectrics such as glass and quartz.

Gubkin et al.\textsuperscript{46} have made a detailed study of the polarization phenomena in polymer electrets. A number of polymers have recently been analytically studied for thermoelectret formation by Perlman\textsuperscript{47} and others\textsuperscript{48}. Pillai et al.\textsuperscript{49} and Pillai and Jain\textsuperscript{50} prepared and studied thermoelectrets made of certain plastics and resins. Fridkin et al.\textsuperscript{51} have prepared thermoelectrets from elastic polymers too.

1.1(c) LIFE-TIME

The life-time of an electret depends upon the properties of the dielectric and conditions of storage. Adams\textsuperscript{52} and Cement\textsuperscript{26} stressed the importance of keeping the electret short-circuited in a dry atmosphere. If kept
open circuited electret shows a decay of charge possibly
due to the accumulation of charges on the surface arising
from ions in the atmosphere.

Groetzinger and Krestch ⁵³ and Groetzinger ⁵⁴
have suggested that the depolarization of a thermoelectret
i.e., decay of its charge with time is due to the motion
of free charges in the thermoelectret under the action of
its internal field. Wiseman and Feaster ⁴² have attributed
the decay of an unshielded electret's charge primarily to
self depolarization by its own internal field rather than
to ion collection.

Recently Perlman and Reedyk ⁴⁷ reported a method
of predicting the life-times of thermoelectrets at room
temperature by extrapolating short charge decay time at
elevated temperatures. The longest lived electrets are
found to be those of K-1 polycarbonate with a life of
thousand years.

1.1(d) THEORIES

(1) Nature of thermoelectret charge

Eguchi's theoretical explanation based on the
assumption of dipole orientation could, however, not explain
the intensity of the observed effect and the reversal of
charges in thermoelectrets. This 'reversal of charges'
observed in large number of thermoelectrets necessitated
consideration of separate mechanism for the formation of
'heterocharge' and 'homocharge'.
(a) Heterocharge

The ideas of Gemant\textsuperscript{26} and Thiessen et al.\textsuperscript{3} on heterocharge have further been developed by Gross\textsuperscript{55} who proposed that the processes of the formation of hetero and homo charges are different. According to him heterocharges are formed by all processes responsible for dielectric absorption such as

(i) hindered dipole orientation (Debye) associated with the rotation of dipole system.

(ii) microphysical heterogeneity of structure (Maxwell-Wegner) associated with the displacement of ions over microphysical distances.

(iii) ionic conduction associated with the formation of space charges.

The first two of these processes do not involve transfer of charge carriers while for the last one this transfer has mirror role to play. The preserved heterocharge is, however, due to 'freezing in' of the volume polarization of dielectric during thermoelectric formation.

Another explanation of volume polarization based on electron trap mechanism has been proposed by Gerson and Rohrbough\textsuperscript{56}. This mechanism successfully explains the observed thermoelectric effect in number of non-polar dielectrics.
(b) Homocharge

Different authors have suggested different explanations for the formation of homocharge at various stages of experimental development of thermoelectret phenomena\(^1,3,26,57,58,59\) but the most accepted one is due to gross\(^60\). Baldus\(^61\) has produced some experimental evidence to show that the homocharge might spread to a certain extent into the dielectric.

(ii) Two Charge Theory

A dielectric when subjected to a high voltage at room temperature has been found to produce two types of surface charges of opposite polarity, one connected with the 'internal' polarization by displacement of ions inside the dielectric and the other connected with an 'external' polarization due to surface effects\(^32\). These polarization formed the two essential elements of the two charge theory by which the electret behaviour is now explained. Adams\(^52\) in the first such theory had considered a slowly decaying volume polarization compensated by free surface charges. During the course of subsequent additional experimental evidence on electret behaviour the terms 'heterocharge' and 'homocharge' were introduced for the surface charge of opposite and similar polarity respectively by Gemant\(^26\). Subsequent improved methods of analysis such as

(i) simultaneous current and charge measurements.
(ii) polarization and depolarization at different conditions in open circuit.

(iii) self depolarization.

(iv) sectioning experiments.

showed that the heterocharge is a 'frozen in' charge and homocharge is a surface charge produced by a surface breakdown or conduction. The implications of the two charge theory have been tested and confirmed by Binder and Wiseman and Phaster. The phenomenological theories have been formulated by Gubkin, Swann, and Asch. Developed a more detailed mathematical discussion of the charge of polarization with time based on rather specific and less general assumptions.

In view of all the evidence available the two charge theory seems to be well established, its main feature being a volume effect associated with dielectric absorption and thus the thermoelectret appears to be a special case of dielectric-absorption.

1.2 FACTORS AFFECTING PERSISTENT INTERNAL POLARIZATION BEHAVIOUR

Characteristics of a polarized dielectrics depend on various factors which are involved in its preparation. Effect of some of these factors are described below:

1.2(a) ELECTRODE MATERIAL

Electrode material and type of contact between
dielectric and metal electrodes decide the nature of charge carriers, e.g., holes or electrons or ions. Contact may be ohmic or rectifying depending on work-functions of the dielectric and the electrode. Pillai et al.\textsuperscript{49} reported a correlation between the electrode material work function and dielectric charge.

In the case of sealing wax Nath and Bhawalkar\textsuperscript{69(A)} have reported that the magnitude of the homocharge varies with the electrode material, when other preparative parameters are invariant. Recently Nath\textsuperscript{69(B)} has reported the dependence of initial surface charge of sealing wax thermoelectrets on the metal electrode work function.

For contact electrification, Wanger\textsuperscript{70} has studied metal insulator contacts. Tin is recommended as the most satisfactory electrode material by many workers\textsuperscript{61,71,72} because it shows less evidence of electrochemical activity than other materials. The effect of different electrode materials on photoelectret characteristics have been studied by Gool\textsuperscript{73}.

1.2(b) POLARIZING FIELD

Charges obtained in electrets are same function of polarizing field\textsuperscript{74,75}. Transition time of charge reversal depends directly on the field strength increases. The polarization along the direction of the applied field is more than that along the perpendicular directions. The observations are in conformity with the experimental data
on electric constants of different waxes reported by Bhadra. Talwar and Khanna have stressed the importance of forming field for the formation of a permanent electret. Nath and Bhawalker have observed the direct dependence of sealing wax thermoelectret charge on polarizing field strength.

1.2(c) POLARIZING TEMPERATURE

Gross has shown that the thermoelectret charges were found to depend greatly on the polarizing temperature of electret forming. Groetzinger-Kretsch and Vanlker-Frolich reported that the electrets prepared at temperatures in the melting region give good results.

Froiman and Fridkin have reported that the increase of heterocharge with temperature can be represented as

\[ Q = Q_0 \exp \left( - \frac{W}{KT} \right) \]

where, \( W \) - Activation energy, \( Q \) - Final charge and \( Q_0 \) - Charge at 0°C.

1.2(d) POLARIZING TIME

The time period during which the dielectric is kept at higher temperature plus the cooling time, under electrical stress is considered as the polarizing time. Good and Stranathan have found the effect of cooling time on the charge density. Yanson showed that a rapid cooling does not form electret.

Wiseman and Feaster reported that the
polarization and the decay of the charge is strongly
time dependent. Recently Bhawalker et al.\textsuperscript{39} have reported
that charge of an electret polarized with the low field
for a long duration is almost the same as the charge of
the electret prepared with high field in short duration
of time.

The dependence of magnitude of the polariza-
tion produced in photoelectret made of anthracen and
( Zn – Cd ) \textsuperscript{S} on the duration of polarization was studied
by Kallman and Rosenberg\textsuperscript{82} who have found that the
reciprocity low is obeyed. This effect was also reported
by Mankov\textsuperscript{83}.

1.2(e) THICKNESS

Bhatnagar and Bhawalker have reported 30%
higher charge for the thermoelectrets thicker than 1 mm
in case where polarizing field exceeded 10 KV/cm. Khanna
investigated the dependence of charge on the thickness of
the electret. The magnitude of the initial hetero-charge
increases as the thickness decreases whereas the maximum
value of the homocharge increases with an increase in
the thickness. Recently, Perlman\textsuperscript{86} studied the effect of
thickness and has observed a slight shift in the peak
position of the discharge current.

Kallman and Rosenberg\textsuperscript{82} have reported that
the residual polarization in photoelectrets rose with
increase of the sample thickness.
1.2 (f) HUMIDITY EFFECT

Wieder and Kaufman\textsuperscript{35} have reported that if electrets are immersed in water the polarization is irreversibly neutralized. It has been observed that unshorted samples exposed to humid surroundings suffer a more serious damage than shorted samples\textsuperscript{26}.

In photoelectrets it has been found that on exposure to humidity, high surface currents are observed which decay rapidly on re-storing.

1.2 (g) RADIATION EFFECT

Gross and Moraes\textsuperscript{55} have investigated the effect of penetrating radiation like X-rays or γ-rays on thermoelectrets.

Effect of illumination on photoelectret characteristics have been investigated by Fridkin\textsuperscript{87} and he has concluded that reciprocity law is obeyed during depolarization. Photodepolarization of photoelectret takes place at a faster rate than dark depolarization.

1.2 (h) SHIELDING EFFECT

Adams\textsuperscript{52} and Gemant\textsuperscript{26} stressed the importance of keeping electrets short-circuited. If the electret is left without shielding the high internal field causes a depolarization of the electret. Gubkin and Skanavi\textsuperscript{88} reported that for ceramic electrets it is not necessary to keep them short-circuited. Later on Pillai and Goel\textsuperscript{89}
have reported the same effect in the case of fluorocarbon thermoelectrets.

Kallman and Rosenberg\textsuperscript{82} have shown the necessity to store photoelectrets dry air. All the photoelectrets studied so far were stored with their electrodes short-circuited.

1.2(1) PRESSURE EFFECT

Sheppard and Stranathan\textsuperscript{90} observed the effect of pressure by observing surface charge characteristics of electrodes under pressure varying from 10 to 288 cms. of Hg. It was observed that the limiting surface charge density is directly proportional to the surrounding pressure. Broughn and Catlin\textsuperscript{91,92} also observed a decrease of charge with lowering of pressure on polymer electrets.

Nadzhakov et al.\textsuperscript{93} have determined the conditions of preservation of polycrystalline anthracene photoelectret in dark. They suggested that if the pressure is increased upto 2 tons/cm\textsuperscript{2}, the photoelectret charge can be preserved for a longer time.

1.3 MEASUREMENT TECHNIQUES

The electrical energy stored in an electret can be determined either by the measurement of the surface charge or by the measurement of the discharge current. First is a non-destructive method and gives valuable informations about the strength, life of an electret and second is a destructive method, which gives
the mechanism of initial polarization of an electret.

1.3(a) SURFACE CHARGE MEASUREMENTS

Eguchi\textsuperscript{94} and Gemant\textsuperscript{26} were the first to use the induction method for surface charge measurement. They measured the effective charge density of an electret with the help of a capacitor and an electrometer. Later on Gemant himself criticized this method and pointed out some of its drawbacks. Sheppard and Stranathan\textsuperscript{90} used same method with slight modifications for charge measurements. Gross and Denard\textsuperscript{95} measured the resultant thermal depolarization current by heating the sample, but this method had a disadvantage that it destroyed the polarization.

Gross\textsuperscript{27} designed a dissectible capacitor for the measurement of surface charge of an electret. This method was found to be effective for electret measurements and has been widely accepted. Gross\textsuperscript{99} later also observed some defects of dissectible capacitor method. As it has a movable upper electrode, the inter space between the electret surface and the electrode increases while lifting the upper electrode. Kakiuchi\textsuperscript{96} improved the induction method and avoided the frictional charges due to surface contact. The upper electrode was fixed and the lower electrode was movable in his arrangement.

Larry et al.\textsuperscript{97} devised a method for making a continuous record of electret strength. Kojima and Koto\textsuperscript{98} measured the surface charges without touching the surface of the electret, by a generating voltmeter. Baumann and
Wiseman\textsuperscript{99} described a method for the measurement of electrical noise pulses in an electret at elevated temperatures. Wild and Stranathan\textsuperscript{4} used an equipment for measuring the equivalent surface charge, which consisted of automatically operated measuring stations with a recorder. Devius and Reynolds\textsuperscript{100} devised a techniques to study the surface charge distributions of electrets by dusting powder on the surface.

Gubkin et al.\textsuperscript{101} have used the various techniques of measurement and have also suggested another method in which charged metallic bodies were placed in the field of an electret and the magnitude of resultant electrostatic interaction was determined. Perlman and Meunier\textsuperscript{102} and Gelin and Stubbs\textsuperscript{103} have used the simple induction method for charge measurement. Sessler and West\textsuperscript{104} have given a correction factor, arising from the unavoidable air gap between metallic electrode and electret. Reedyk and Perlman\textsuperscript{105} have used an improved induction technique to avoid the effect of air gap in their experiments.

Cross and Hart\textsuperscript{106} have given an alternate method for studying the electret characteristics by measuring the microscopic dipole moment of an electret with the help of a torsion balance. Recently Pillai and Jain\textsuperscript{107} have published a comprehensive review of surface charge measurement techniques.
1.3(b) DISCHARGE CURRENT MEASUREMENTS

Frei and Groetzingen\textsuperscript{108} suggested second method of measuring the thermo-electret charge. Groetzingen and Kretsch\textsuperscript{53} used for the first time, the method of thermal depolarization current for thermoelectrets. Recently developed 'thermally stimulated discharge current (T S D C)' technique has been used by numerous workers such as Perlman and Creswell\textsuperscript{48}, Turnhout\textsuperscript{109}, Lilly et al.\textsuperscript{110}, Pillai et al.\textsuperscript{111}, Gross\textsuperscript{112}, Caserta and Serra\textsuperscript{113}, Tilley\textsuperscript{114}, Perlman\textsuperscript{86}, Reedyk and Perlman\textsuperscript{105} and others\textsuperscript{86,115}.

Nadzakov\textsuperscript{6} and Fridkin\textsuperscript{116} have suggested methods of measuring discharge current in photoelectrets. Later on several workers such as Zheludev and Fridkin\textsuperscript{117}, Silver\textsuperscript{118}, Fridkin\textsuperscript{119}, Kallmann and Rosenberg\textsuperscript{82} and Fridkin et al.\textsuperscript{120,121} have proposed different techniques for the measurement of internal polarization, as depolarization current.

1.4 PHOTO DEPOLARIZATION

As already pointed out earlier Nadzhakov\textsuperscript{122,123} discovered a new type of electret effect known as photo-electret effect. He observed photo-conduction space charges accumulated in polycrystalline sulfur and that these charges were retained for long time after illumination ceased and the applied electric field was removed.

Although photo-conductivity is a necessary condition for exhibiting photoelectret effect, the sufficient condition is the existence of at least partial trapping of
both kind of charge carriers in the bulk of the material. Photoelectrets of polycrystalline sulfur exhibited a stable heterocharge, and no charge of photoelectret polarity was observed.

The charge carriers are generated near the illuminated electrode, they get separated under the action of applied electric field and are subsequently trapped in the bulk thus polarizing the material. The polarization is uniformly distributed in the photoelectret. Although, thermo- and photo-electret states are produced in the materials under different experimental treatments, they have several features in common.

1.4(a) MATERIALS CAPABLE OF SHOWING PHOTO-ELECTRET EFFECT

Many workers reported the photo-electret state of inorganic photoconductors like sulfur, sulfur, calcium sulphide, zinc sulphide, mercury iodide and silver chloride. Recently workers have shown the photoelectret effect in the ferroelectric semiconductors like SbSI and SbSBr.

Beside inorganic materials the photoelectret state has also been observed in organic materials like Anthracene, Chryscene, I - Bromoanthracene, naphthalene, pyrene and some others aromatic hydro-carbons.

1.4(b) LIFE TIME

Investigations of the depolarization of photoelectrets and the dependence of their life-times on the
conditions of polarization are important. The photoeletrets should be stored in dark and in dry air with their electrode short circuited.

Nadzhakov and Kashukeev\textsuperscript{150} found that the duration of the retention of photopolarization in polycrystalline sulfur and the decay of this polarization with time depend on the purity of the dielectrics and on the thermal conditions during the various treatments. The decay can be represented by the relation\textsuperscript{150}.

\[ P_0 - P = at^n \quad (n>0) \quad (1.2) \]

where \( P_0 \) is the initial value of the photo-electret polarization, \( P \) is the polarization at the time \( t \), \( a \) and \( n \) are constants. Further Kallman and Rosenberg\textsuperscript{82} showed that the decay law for the photoelectrets in darkness depends not only on the dielectric material, but also on the polarization field intensity, the sample thickness, the nature of illumination used during polarization and on other conditions.

The results of Fridkin and Zheludev\textsuperscript{117,118} on mono-crystalline sulfur and on mono-crystalline anthracene have been found in agreement quite well with those obtained by Nadzhakov and Kashukeev\textsuperscript{150}. In case of monocryystals of sulfur and anthracene, decay of polarization in dark obeys an exponential law -

\[ \sigma = c \exp\left(-\frac{t}{\tau}\right) \quad (1.3) \]

where \( \sigma \) is the initial photoelectret charge, \( \sigma \) is the photoelectret charge at time \( t \) and \( \tau \) is the relaxation
time. Decay of polarization in darkness in polycrystalline photoelectrets does not obey an exponential law.

It is possible that the initial rapid decay of polarization of polycrystals in darkness represents the liberation of electrons from shallow levels, while the subsequent slow decay is due to the liberation of electrons from deeper levels. A stable residual polarization in polycrystalline photoelectrets is due to the localization of electrons at the deepest levels, related possibly to grain boundaries.

1.4(c) THEORIES

Phenomenological theories of photoelectret have been proposed by Kallman and his co-workers\textsuperscript{82,151,152}, Fridkin and Zheludev\textsuperscript{153}, Chetkarov\textsuperscript{154} and Adirovich\textsuperscript{155}.

(1) MODEL OF POLARIZATION

Experiments by many earlier workers show that two fundamentally different internal charge distributions can develop, barrier and bulk polarization. In the former the free positive and negative carriers accumulate near the electrodes because of high resistive layers at the photoconductor-electrode interfaces. If these two resistive layers are of the same magnitude then barrier polarization leaves the sample electrically neutral.

In bulk polarization, the more mobile carrier are at least partially removed from the sample with less mobile carriers remaining in a uniform distribution over the bulk
of the sample.

Barrier polarization requires resistive layers at the electrodes, the resistance of the sample for the less mobile charges. Bulk polarization occurs when this condition is not satisfied and additionally the sample is nonuniformly excited.

(iii) CHARGE LAYER MODEL OF POLARIZATION

The model\textsuperscript{156} used is of a macroscopic nature consisting of localized charge layers which may not be infinitesimally narrow, indeed the whole picture of bulk polarization is built upon a charge layer of one sign which may extend across a greater part of the sample. The model assumes that the nature of the charge distribution is determined to a large extent by high resistive layers, in the case of barrier polarization by those near the electrodes.

(iii) BARRIER POLARIZATION

The barrier polarization is based upon two fundamental observations, firstly with the barrier polarization a discharge is never observed in the $d_1$ or $d_2$ region figure (1.1) and secondly, the experiments with samples of various thickness show that density of charges depends only upon the applied polarizing voltage and not on applied field. These results can only be interpreted in terms of thin charge layer accumulations.

Two possible types of charges separation can be visualized in powered or semicrystalline samples. Either there
Fig. 1.1: Double charge layer model of a polarized photoelectric.

Fig. 1.2: General model of bulk polarization.
is a polarization of single grain or across the whole sample.

According to the model developed for barrier polarization maximum charge density (σ maximum) for a given polarizing voltage (V₀) should be independent of the polarizing light intensity. Only the rate at which the charge separation occurs should depend upon this intensity. Any radiation which produces free charges in the photoconductor also discharges polarization.

The dark decay of polarization is brought about by thermal release of trapped charges. Not only the polarization charges Q⁺ and Q⁻ decay in time, but free charges are also created in the d₂ region. All of freed charges move in a direction so as to diminish the existing polarization.

(iv) BULK POLARIZATION

When the resistance of the sample is comparable to the barrier resistances, bulk polarization is possible. The general model of bulk polarization is given in figure (1.2). Figure shows that for which the negative carriers are assumed to have the highest mobility, positive charges are distributed over the whole bulk of the sample, E' goes through zero some where in the middle and reverse release is possible in the d₃ region, provided the releasing radiation is restricted to this depth.

The charges of higher mobility will also give rise to a charge accumulation directly at the surface of
maximum excitation, the magnitude of which depends on the case with which these charges can move out of the sample. The sample becomes charged with the sign of the less mobile carriers if the barrier at the left is smaller than the total resistance of the sample including the barrier at the right. If the more mobile charges would not move out of the sample at all, no d.c. current would flow at the equilibrium of polarization built up.

1.5 CONDUCTION IN ORGANIC SOLIDS

The experimental data collected by studying the electrical conduction of any new type of material is used to interpret carrier generation, trapping & transport mechanism in it.

1.5(a) CARRIER GENERATION MECHANISM

(1) CARRIER GENERATION IN THE DARK

The generation of carriers in organic solids give a relation of dark conductivity

\[ \sigma = \sigma_0 \exp \left( - \frac{E_a}{kT} \right) \quad (1.4) \]

which suggest that the carriers were of intrinsic origin and thus the experimental activation energy \( E_a \) could be equated to half band gap \( E_g \). Early workers suggested that \( 2E_a \) is the same as the energy of the lowest excited singlet state \( 1E \), while for several hydrocarbons \( E_a \) values were found to be one half the lowest excited triplet state energy \( 3E \). However there are two very severe objections to the singlet or triplet state theories :-
(A) Gutmann and Lyons found that for large number of organic solids, there is a very little agreement between $2E_a$ and either $1E$ or $3E$.

(B) Theoretically also, there is no justification why $E_a$ should be related to either $1E$ or $3E$ by equation of intrinsic semiconduction.

The other possibility of generating carriers is by injection. It has been shown that both the holes and electrons can be injected into an organic solid. Kallmann- and Pope$^{141}$ and Adolphe et al.$^{157}$ have found the hole injection in Anthracene. Electron injection in Anthracene has been achieved by Buchen and Nehl$^{158}$.

(11) CARRIER GENERATION IN LIGHT

There is no simple explanation of the photogeneration of carriers in organic solids. The optical absorption properties of organic solids can be fully described in terms of Frankel excitons only, but still in view of the reportedly small gain of photo-excited carriers, carrier generation via the low probability mechanism of direct band-to-band transition is not totally prohibited. Castro and Harning$^{159}$ and Chaiken and Kearns$^{160}$ have indeed provided experimental evidence for this mechanism in the region $2500 \text{ A}^0 - 3000 \text{ A}^0$. Silver and Sharma$^{161}$ have given the theory of this process. Kepler$^{162}$ found the number of photocarriers in the wavelength region $3400 \text{ A}^0 - 4100 \text{ A}^0$ to depend very sensitively on the condition of the crystal surface.
which is what should be expected in the type of mechanism.

The carriers may also be produced via excitation interaction between two singlet excitons, the same of whose energies is sufficient to excite an electron-hole pair$^{163}$. Hosegawa and Yoshimura$^{164}$ found the photocurrent to vary as fourth power of incident light intensities. At higher light intensities carrier recombination effects were very strong which reduced the fourth power dependence of a square law one. Jortner$^{165}$, Choi$^{166}$ and Schott$^{167}$ who have concluded the rate constant for the process of polarization of excitons. Coppage and Kepler$^{168}$ in contrast to Hasegawa and Yoshimura (loc. cit.) found the photocurrent to vary as cube of the incident light intensity. Recently Hirth$^{169}$ reported the generation of electrons and holes in solid and liquid benzene by strongly absorbed light.

(iii) SCHOTTKY EMISSION AND POOLE-FRENKEL EFFECT

The nature of the current I limited by the height of the barrier at the electrode is given by

$$I = AT^2 \exp \left( - \frac{\phi}{K T} \right) \exp \left[ \frac{e E}{\varepsilon \varepsilon_0} \right]$$

---(1.5)

where $e$ is the electron charge, $T$ - absolute temperature, $K$ - Boltzmann constant, $\phi$ - the barrier height (eV), $A$ - Richardson constant, $\varepsilon$ - the dielectric constant, $E$ - the electric field strength at the electrode.

Thus the current $I$ depends both on $\exp \left( \sqrt{E} \right)$ and temperature $\left[ I \sim T^2 \exp \left( - \frac{\phi}{K T} \right) \right]$. The equation (1.5)
is valid only for an ideal dielectrics (without traps).

Now a theory has been developed\(^{146}\) for dielectric with traps. Thus the Schottky emission especially for the highest field cannot be completely excluded and must be considered as a process cooperative with the thermal injections of charge carriers. Recent observations by Srivastava and Tomar\(^{147}\), Lengyal\(^{172}\), D'wyer\(^{146,148}\) and Lilly and Mc. Dowell\(^{30}\) also support this. Besides this, large number\(^{173}\) of amorphous appearing insulators have also been found to exhibit linearity on Schottky plots.

Poole-Frenkel effect is similar to Schottky emission. The only difference is that the electrons are excited thermally from traps into the conduction band of the insulator. Due to immobility of the positive charge associated with the trap, barrier lowering in Poole-Frenkel effect is twice that in case of Schottky effect.

\[
I = AE \exp \left( - \frac{\varphi_b}{2KT} \right) \exp \left[ \frac{e}{KT} \left( \frac{eE}{\varphi_b} \right)^{1/2} \right] \quad (1.6) \]

where \(A\) is a constant and \(\varphi_b\) is the barrier height.

(iv) SPACE CHARGE LIMITED CURRENT CARRIER INJECTION

Space charge limited currents (SCLC) are important, because injected current is independent of the mechanism of carrier generations and depends only on the transport and trapping of the carriers within the crystals. The injected charge carriers of one sign may cause the
appearance of SCLC. The character of SCLC is defined by the density distribution of the trap levels in the band gap\textsuperscript{174-176}. The theory of unipolar SCLC was previously developed by Rose\textsuperscript{177} and Lampert\textsuperscript{178}.

The SCLC theory without the assumption of the blocking electrodes was proposed by Muller\textsuperscript{179}. Recently the existance of SCLC and influence of electrode material and that of temperature in many organic solids have been reported by Sworakowski\textsuperscript{180} and Szymanski et al.\textsuperscript{181,182} and Thomas et al.\textsuperscript{183}. Recently Singh and Srivastava\textsuperscript{184} have accounted for SCLC following a square law in case of naphthalene at higher voltages.

1.5(b) CARRIER RECOMBINATION AND TRAPPING

A local excess concentration of carriers vanishes by two processes :- (1) Leakage out of the region by diffusion (2) and decay by hole-electron recombination. Both the generation and recombination of electron-hole pair occur simultaneously in semiconductors and in equilibrium the two rates of holes recombination may be written in terms of kinetic theory as

\[ r = N \sigma V \]

where \( N \) and \( \sigma \) are respectively the density and cross-section of recombination centers and \( V \) is the diffusion velocity of holes.
Recently Batt et al.\textsuperscript{185} have reported carrier recombination through the field dependence of carrier generation process and Schott\textsuperscript{186} through ionization by high energy particle while Mehl and Funk\textsuperscript{187} have found radiative recombination at room temperature. Thomas et al.\textsuperscript{188} have evaluated trap densities in crystals prepared by different procedures. Sworokowski\textsuperscript{189} has successfully calculated theoretically the trap depths for holes and electrons in anthracene crystals doped with anthraquinone and tetracene. Discrete\textsuperscript{190} as well as exponentially\textsuperscript{191} distributed trapping levels have also been found.

1.5(c) MECHANISM OF CARRIER TRANSPORT

The earliest electronic conduction theories were directed towards an explanation of conductance rather the mobility. Electronic conductivity in organic solids has been widely accepted\textsuperscript{192-197}. The results from the application of the band theory to organic solids are in disagreement with the experiments. Further modification of the band models\textsuperscript{198} have been given to explain the measured mobility value.

1) HOPPING MODEL

A simple hopping model was applied to the motion of ions in ionic crystals by Seitz\textsuperscript{199} and a similar treatment has been applied by Pohl\textsuperscript{200} and by Pohl and Opp\textsuperscript{201} to the motion of carriers in an organic solid. The carrier are considered to move by hopping to neighbouring molecules in a manner which is random except for the anisotropy caused by the applied field.
The intermolecular coupling in an organic solid is weak and the observed mobilities small, which suggests the application of hopping model to charge transport in these crystals\(^{201}\). Le Blanc\(^{202,203}\) suggests that transport would be described by hopping model in the polycrystalline or amorphous organic materials where as conventional band theory should apply to pure organic solids in the crystalline form. Recently Siebrand and Munn\(^{204}\) have developed charge transport theory for organic solids.

**(ii) TUNNEL MODEL**

Two related mechanism for semiconduction in molecular crystals were proposed by Eley, Parfitt, Perry and Taysum\(^{205}\) in 1953. Later on this model led to proposition of semiconduction in molecular crystals by Eley et al.\(^{206-213}\).

The potential barrier between the molecules under the influence of an external electric field is covered through which the electron and/or the holes can then tunnel to occupy the corresponding orbitals in the adjacent molecules. Since the model involves the tunneling of a charge carrier away from an oppositely charged site, the tunneling particle remains bound to hole until the coulombic energy between them has reduced to a value \(\sim kT\). This situation will be obtained after the electron has tunneled over a distance of several lattice spacings.

It can be seen from the above that the study of electrical conductivity variation with field, temperature and
electrode material, can not provide experimental data for understanding carrier generation and their mode of transport. Besides this the polarization processes occurring in the material when at higher temperature in the presence of field may affect the generation and transport of charge carriers\textsuperscript{214}. As Gutmann\textsuperscript{312} has already pointed out that correlation between activation process in electrical conduction and dielectric relaxation exists, so it becomes necessary to undertake a systematic study of polarization in the substance. Study of thermoelectret state provides satisfactory experimental data for the same.

1.6 DIELECTRIC CONSTANT AND LOSS ANGLE TANGENT

From what has been said above it can be seen that thermo electret state in any semi-insulator may be due to frozen polarization consisting of (i) oriented dipoles (ii) microscopically displaced ions (iii) microscopically displaced and trapped charge carriers of the crystallite boundaries and at trapping centers which may arise due to ionized impurities and molecules of the host material. On the other hand photo-electret state is entirely due to the trapped charge carriers which are generated either by the direct interaction of the radiation with the molecules of the solid at the surface or due to exciton mechanism which may diffuse in the bulk and subsequently disintegrate into pair of charges.
Thus the study of photodepolarization may be used to draw inference about the nature of the trapping centres for charge carrier and their modes of transport. Further information about the nature of polarisation connected with carrier mechanism at high temperature can be obtained from the dielectric constant variation with temperature and frequency. The brief review of the report on dielectric behaviour is given below.

The dielectric constant of a material depends strongly on the frequency of the applied field and the temperature. Chatterji and Bhadra observed three times increase in dielectric constant of carnauba wax, thermoelectric as compared to unpolarized sample. Wikstrom and Wiseman et al. studied the polarized and unpolarized carnauba wax and found no change in dielectric constant and loss angle tangent. Fuoss and co-workers have reported good amount of work on high polymers. High polymers containing polar groups show more or less orientational polarization due to change in orientation of molecular segments in an externally applied field. Their dielectric constants are low and almost independent of frequency and their dielectric losses are very small.

Roberts and Rohrbourgh studied the complex dielectric constant from room temperature to liquid wax temperature in the frequency range of 50 c/s to 13 kc/s. Gubkin and Skanavi could not find any change in dielectric constant over a period of twenty days in case of CaTiO3 and
SrTiO₃. An isotropic change in the value of dielectric constant of polarized and unpolarized sample was obtained by Mc Mohan in the case of some organic materials. Elgard studied the dielectric properties of ferroelectrics subjected to an electric field and found that the function $\varepsilon = F(E)$ and $\tan \delta = F(E)$ in the direction of the field differ considerably from that in the perpendicular direction to the field. Graham William reported the dielectric properties of polymethyl acrylate and amorphous polyethylene terephthalate.

Recently Srivastava and Bhatnagar showed that the value of dielectric constant of sugarcane wax is increased by a very small amount on application of the d.c. field. Jangvir Singh has found that the dielectric constant of β-naphthol thermoelectret is maximum just immediately after the polarization of the sample and then it decays and returns to its normal value corresponding to that of unpolarized sample.

1.7 STATEMENT OF PROBLEM

More experimental data on new dielectric is needed to test the validity of electron trapping in deep traps and/or orientation of molecules within the dielectrics which are said to be responsible for formation of homocharge or heterocharge. Organic molecular crystalline dielectrics appear to be quite promising in this respect. With this view
point a new organic molecular crystalline dielectric (acenaphthene) a product of Fluka AG. Buchs SG made in Switzerland was selected for the present work. An extensive study was performed in following major part.

(1) Electrical conductivity in an organic semiconductor is found to depend on structural charges which lead to its variation with temperature. Studies of the variation of conductivity in impure and zone refined acenaphthene have been carried out as a function of (i) temperature and (ii) field. An attempt has been made to assign a plausible mechanism of conduction in acenaphthene.

(2) Study of surface charge measurements and depolarization current of thermoelectrets prepared at various polarizing fields and polarizing temperatures have been carried out to understand the physical mechanism of electret formation and also to understand dipolar, ionic and electronic processes occurring in acenaphthene during polarization.

(3) In order to investigate any dipolar orientation as a possible cause of the formation of hetero-charge, dielectric constant has been measured in thermal equilibrium condition. Study of temperature and frequency variation of dielectric constant has also been undertaken.

(4) The depolarization current characteristics of the photoelectrets of acenaphthene have been studied under different polarizing conditions as function of dark
field polarization, photo-field polarization and field reversal polarization. This enables one to understand the idea of electron trapping in deep traps. A comparison study of these modes of decay has been discussed.

(5) Finally results of these studies have been analysed in the light of the available literature on the subject, so as to arrive at some conclusion mentioned at the end of this thesis.
Structure of Acenaphthene $C_{12}H_{10}$