# ELECTRICAL SWITCHING STUDIES ON THE THIN FILMS OF POLYFURAN AND POLYACRYLONITRILE PREPARED BY PLASMA POLYMERISATION AND VACUUM EVAPORATED AMORPHOUS SILICON

ABRAHAM, P. K.

THESIS SUBMITTED TO
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
FOR THE AWARD OF THE DEGREE OF
**DOCTOR OF PHILOSOPHY**

THIN FILM DIVISION
DEPARTMENT OF PHYSICS
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN - 682 022

JULY 1989

DEDICATED

TO

MY PARENTS

## DECLARATION

I hereby declare that the work presented in this thesis is based on the original work done by me under the guidance of Prof.K.Sathianandan in the Department of Physics, Cochin University of Science and Technology and has not been included in any other thesis submitted previously for the award of any degree.

Cochin 682022

7 July 1989

ABRAHAM, P.K.

# CERTIFICATE

Certified that the work presented in this thesis is based on the original research done by Mr.Abraham, P.K. under my guidance in the Department of Physics, Cochin University of Science and Technology, and has not been included in any other thesis submitted previously for the award of any degree.

Cochin 682 022
July 7, 1989

Dr.K.Sathianandan
Professor of Physics
(Supervising Teacher)

# ACKNOWLEDGEMENTS

Thanks are also due to the technical, administrative and library staff of the Department of Physics and staff of the University Science Instrumentation Centre for the help and cooperation I have received from them. I also acknowledge with thanks Cochin University of Science and Technology for providing me with a junior/senior fellowship during the period of my research.

I take this opportunity to acknowledge my beloved wife Valsa for the constant endurance and help rendered to me during the entire period of my research work, without which it could not have been possible to complete this work.

Finally, I am thankful to Mr.Sasidharan for neatly typing this manuscript.

# PREFACE

The growth of science and technology is heading towards a molecular or even to a submolecular level of engineering. Nowadays, scientists hope of building 'molecular computers' which would in turn be as good as human brain. The growth of solid state physics from single crystal to thin film stage was rapid and spectacular. Thin amorphous films are also now in the forefront of application after passivation. The thin film technology gave an impetus to the growth in every field of frontier applications such as microelectronics, superconductivity, solar cells, optical, magnetic and metallurgical coatings, integrated optics and so on. These are used in communication, space technology, engineering, medicine and in various other fields of science and technology. The progress in miniaturisation is already achieved in the nanometric dimension.

The theme of the present thesis is electrical switching studies on a few thin films of polymeric materials and amorphous silicon. It is possible that polymeric materials would be the future substitute to most of the present materials. This is evident from the stupendous growth of applications found in the last decade.

An electrical switching device has two electrically distinct states. One is a conductive ON state in which electric charges are allowed to flow through it and the other is a nonconductive OFF state. These two distinct electrical states form the basis of the digital representation--the binary coding. The ON and OFF states of a switch by convention represent the 'one' and 'zero' states and are used in computer address systems. The investigations of switching in polymeric thin film materials are carried out in the hope that stable switching may be observed which in turn may be used as a cheap memory device in place of sophisticated devices.

In spite of the large volume of work that emerged in the area of switching using inorganic materials, switching in polymers are not widely investigated. The polymer properties can be easily changed by tailoring with different functional radicals and also depend on the method of preparation. With this aspect, stable switching properties are expected in many polymers and a series of investigations are carried out to examine closely the switching behaviour of a few polymer films. In the present work, switching studies of plasma polymerised polyfuran, polyacrylonitrile and evaporated amorphous silicon thin films are presented. The results and possible explanations are given. The thesis is presented in six chapters.

The first chapter is a general introduction to the electrical switching in thin films. This includes the history of development of the switching in thin films and the present status. The electroformation and the Mott transitions are described to understand the switching phenomenon. Various related aspects such as negative resistance and memory to switching are accounted in this chapter. The parameters that are used to characterise the phenomenon like the threshold voltage, time response to a voltage pulse and the ON state of a switch are described. The working of a switching transistor is described and compared to that of a thin film switch. The mechanisms like thermal, electrothermal and purely electronic phenomena found in switching are given in detail. Finally the scope, the feasibility and the importance of polymer thin films in switching are highlighted.

The second chapter describes polymers, polymerisation and all the associated experimentation. Various methods of preparation of thin films by plasma polymerisation are briefly described. A general description of electrical and electronic behaviour of polymer films are included. The fabrication of a sweep voltage which is used in the investigation is described. The design and fabrication of a vacuum chamber is also given. The preparation of electrodes and the technique of evaporation used in a coating unit are briefly covered.

This chapter also deals with the experimental set up used for switching investigations.

The third chapter deals with the details relating to the preparation of thin films of polyfuran by audio frequency and radio frequency plasma polymerisation. The memory switching investigations are presented. This covers the general current-voltage characteristics, the dependence of threshold voltage on film thickness and film temperature, the temperature coefficient of resistance and the activation energy. The results and discussion are presented. The mechanism of switching is due to the formation of conducting channels in both audio frequency and radio frequency polymer films.

Chapter four mainly deals with the switching investigations of an audio frequency plasma polymerised polyacrylonitrile thin films. The method of film preparation, the growth rate and the possible structures are initially discussed. The dependence of threshold voltage on film thickness and temperature is described. The temperature coefficient of resistance and the activation energy in the ON and OFF states are presented. The analysis of the current-voltage characteristics in these films show that the switching is due to space charge effects. In this chapter the investigation of switching characteristic of direct current discharge plasma

polymer films are also included. The AF and DC thin film switching characteristics are compared. The variation of capacitance with voltage and the variation of ON state resistance are also included. Subsequently results and discussion are presented.

The fifth chapter describes switching in amorphous silicon thin films. The preparation of silicon films by evaporation from a tungsten filament and by electron beam gun source are given. The switching in these amorphous silicon films are reported. The effect of film thickness and temperature on the switching threshold voltage is discussed. A comparison of properties is made between electron gun evaporated and filament evaporated silicon thin films.

In the sixth chapter a summary of the work and the results in the preceding chapters are given. Both filamental and electronic mechanisms are discussed and summarised. Part of the investigations presented in this thesis has been presented/published in the form of the following research papers:

1. Switching behaviour of plasma polymerised polyfuran films. Thin Solid Films, 164 (1988) 353.

2. Memory switching and conduction in plasma polymerised acrylonitrile thin films.

   Indian J.Phys. **63A(5)** (1989) 525.

3. Switching properties of vacuum evaporated amorphous silicon thin films.

   Proceedings of the Solid State Symposium, BARC, Bombay, December 27-31, 1987, Vol.30C.

4. Investigations on the switching behaviour of amorphous silicon and certain polymer thin films.

   16th O.S.I. Symposium on Optical and Optoelectronic Applied Sciences and Engineering, 1987.

5. Electroforming, negative resistance and memory switching of thin plasma polymerised hexamethyl-disiloxane films.

   Abstracts of XIX National Seminar on Crystallography, December 18-20, 1987.

6. Switching and bistability in D.C.plasma deposited polyacrylonitrile thin films.

   National Symposium on Electrochemical Material Sciences, 1988.

# CONTENTS

# Chapter 1

## ELECTRICAL SWITCHING IN THIN FILMS

## Abstract

A general introduction to the switching and allied phenomena is presented. Subsequently, developments of switching in thin films are described. The Mott transition is qualitatively presented. The working of a switching transitor is outlined and compared to the switching observed in thin films. Characteristic parameters of switching such as threshold voltage, time response to a voltage pulse, and delay time are described. The various switching configurations commonly used are discussed. The mechanisms used to explain the switching behaviour like thermal, electrothermal and purely electronic are reviewed. Finally the scope, feasibility and the importance of polymer thin films in switching are highlighted.

1

## 1.00 INTRODUCTION

Ever since the invention of the flow of electric charges, a make and break contact has been in common use. A switch forms an integral part of any device. This represents two states-one is a highly conducting ON state and the other a non-conducting OFF state. Thus two electrically distinct states are possible in a switch. The significance of these two states is that they form the basis of the digital language in the binary coding with zero and one states representing the OFF and ON states of a switch. This enables unlimited expansion in the electronic scenario.

Switching in the broad sense is a reversible process between the ON and OFF states. This could be achieved in materials by various means using electrical, thermal and light energy. The switching states are obtained by working between a high resistance and a low resistance or a low current and a high current or a high voltage and a low voltage. A simple switch is a mechanical contact that can be closed or kept open. With the development of vacuum tubes, the switching phenomenon is realized without a moving mechanical part. The conducting path through the vacuum tube is achieved by the ionisation of the gas in the tube. The ionised conducting plasma is formed at a particular threshold field. As the

field is lowered below the threshold the tube ceases to conduct. The simple gas diode is an example of threshold switching. One other type of switching is the memory switching. In this, the change of state is retained even after the removal of the applied field. This memory is reverted by using another suitable electrical pulse. Threshold and memory switching are widely used in electrical circuits for communication and registration of information respectively.

Very early reports of a switching like phenomenon was observed in the case of vaseline [1]. In early seventies there was considerable upsurge of research in this field especially in inorganic materials. In 1967, Simmons and Verderber [2] observed a 'forming process' in $Al-SiO_x-Au$ sandwich configuration. After the forming process the conductivity of the specimen rose by many orders. Infact, permanently enhanced conductivity was found after the forming process. In 1968, Ovshinsky [3] found that the dynamic resistance changed monotonously with the applied bias and when the current was lowered the film switched back to high resistance state.

The mechanisms of traffic (communication) and storage (memory) of information in living beings could have close identity with the mechanisms of switching in materials. The

investigation of switching in materials would unravel new

horizon of knowledge about intelligence. The threshold

switching represents the traffic of information from one

point to other while the memory switching represents the

storage of information. The investigation of switching

studies in this context is justified both for understanding

the mechanism involved and in developing a superior techno-

logical device.

Memory or threshold switching is observed in a

variety of materials of both organic and inorganic origin.

This is observed in elements, compounds, complex materials

and polymers. Crystalline and amorphous materials exhibiting

insulating or semiconducting properties are found to show

switching behaviour. The mechanisms of switching are found

to be different in different materials. Filamental, phase

change, thermo-electronic and purely electronic process are

used to explain the switching behaviour observed in different

materials.

The early reports of switching are mainly in chalco-

genide glasses and oxides [4-7]. Switching is also observed

in elemental selenium [8] boron, silicon, germanium, [9]

complex molecules [10,11] and long chain polymers. This

phenomenon is also reported in several heterojunctions [12-14].

In certain cases, polarity dependent switching is found to

occur. The switching would take place for a particular polarity. If the polarity is reversed the impedance would rise corresponding to the OFF state. Such polarity dependent switching is reported in the cases of a-Si/$In_2O_3$-$SnO_2$ thin film junctions [15] , Silver photo doped $AS_2S_3$ films [16] and $Ag_2Se$/Se/M structures [17].

The invention of the transistor [18] made a revolution-ary growth in electronics. Switching devices like transistor, field effect transistor and multivibrator came into reality. The rapid growth in this field took new dimensions with integrated circuits employing multifunctions along with switching action. In this context, a study of the switching action in a transistor would give a proper understanding and comparison with thin film switching devices. The investigations in thin film switching devices are being carried out with the hope that these simple thin film devices may find use in computer and other electronic memory devices. In fact, an application in a computer is reported by Tauc [19].

## 1.10 SWITCHING TRANSISTOR

A switching transistor is designed to function as a switch that can change its state from high voltage low current (OFF) to a low voltage high current (ON) state in a very short

time. The basic modes of operation are the current mode and the saturated mode. The minority carrier concentration (electrons) and the majority carrier concentration (holes) are shown (Fig.1.01 a,b,c) in the base region for cut off, active, and saturation regions for a PNP transistor. From fig.1.01 d we see that the transistor is in the cut off, active, or saturated region depending on the base current $I_B$ and the collector voltage $V_{CE}$. For higher values of the base current say 2 m.A small collector voltage increase due to signal, will switch the transistor to the ON state. The transistor is now in the saturated region of operation. For lower values of the base current the transistor never reaches the saturation region even for higher values of collector emitter voltage.

For the cut off region, the collector current is OFF and the collector junction is reverse biased. For the active region II, the emitter is forward biased and the collector is reverse biased. For the region III both collector and the emitter are in the forward biased region. In this saturated mode the transistor duplicates the function of an ideal switch. In the cut off region the collector emitter terminals are virtually open. In the ON state, that is in the saturated region, the collector emitter resistance is even less than 10 Ohms. We see that the charge density in the base region
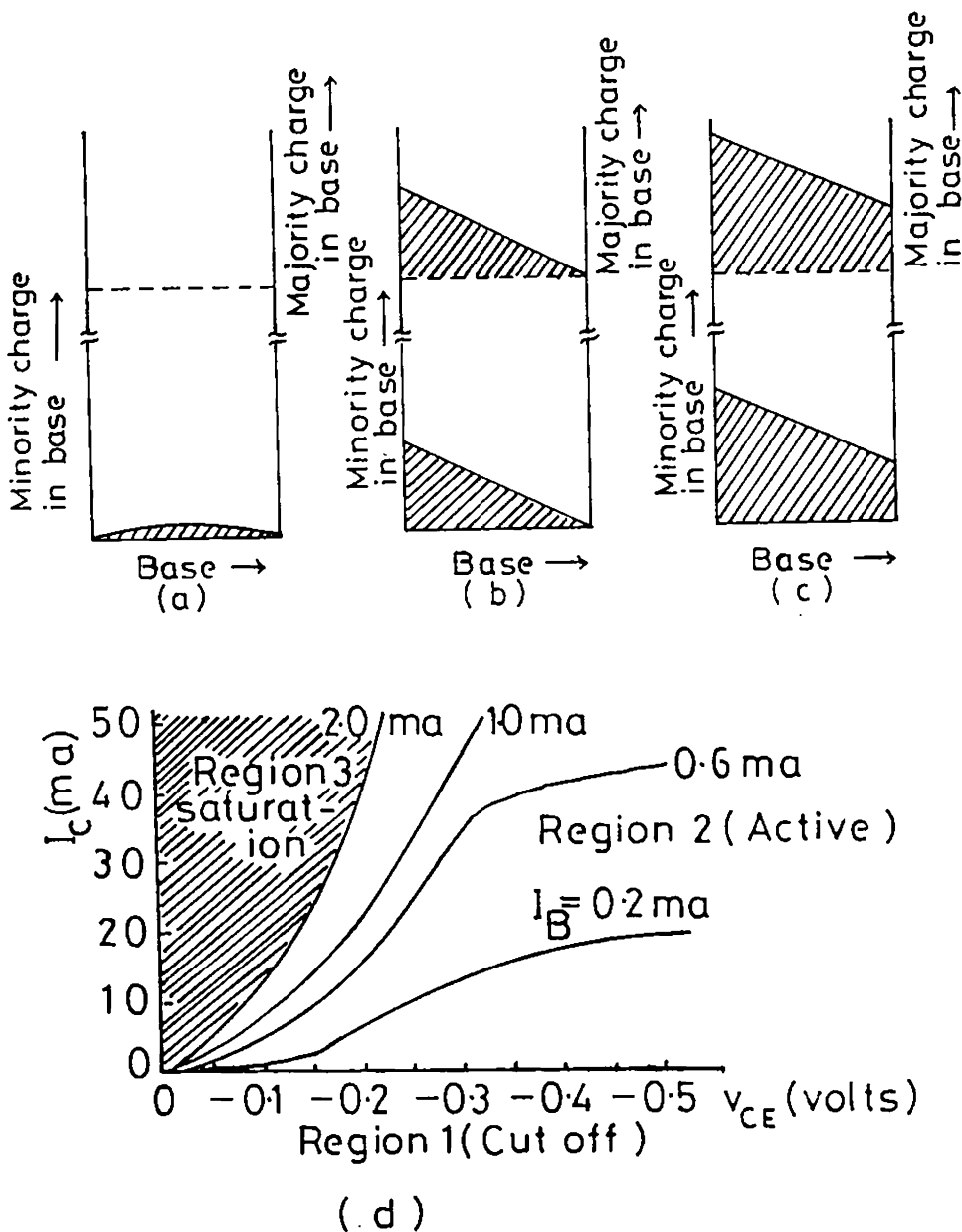
Fig.1.01  The minority and majority charge distribution in the
base region of a PNP transistor.
(a) When both the collector-base and emitter-base junctions
are reverse biased (cut off region of operation).
(b) emitter-base junction forward biased and collector
base junction reverse biased (active region of operatio
(c) both emitter-base and collector base junctions are
forward biased (saturation region of operation).
(d) Grounded-emitter collector characteristic of a PNP
transistor showing the cut off, active and saturation
regions of operation.

becomes high and saturated allowing the collector and

emitter to be in the closed on state. This high charge

density acts as if the transistor is also a piece of conductor

with free carriers [20,21]. Coming to the switching action

in insulating and semiconducting films, for a comprehensive

comparison with the transistor switching, an examination of

some of the close phenomena like 'forming process' and 'Mott

transition' are required. This will furnish more insight into

the switching in a simple thin film.


1.20   ELECTROFORMING

Electroformation, in general, is a fore-running

process of switching. The terminology was coined by Hickmott

[22]. Many of the insulator films undergo a large permanent

increase in the conductivity by the application of a forming

voltage. Formed films showed properties like threshold

switching, voltage controlled negative resistance, current

controlled negative resistance, electroluminescence and

temperature independent conductivity. These are reviewed

by Dearnaley et al. [7]. Electroforming is reported in many

oxides [23], halides [24], polymers [25-27] and sulphides [28].

Verderber and Simmons [2] have given a thorough account of the

forming process in SiO films. The conductivity before and

after forming is as shown in Fig.1.02. The conductivity of a

formed sample is many orders greater than the conductivity

of an unformed sample.
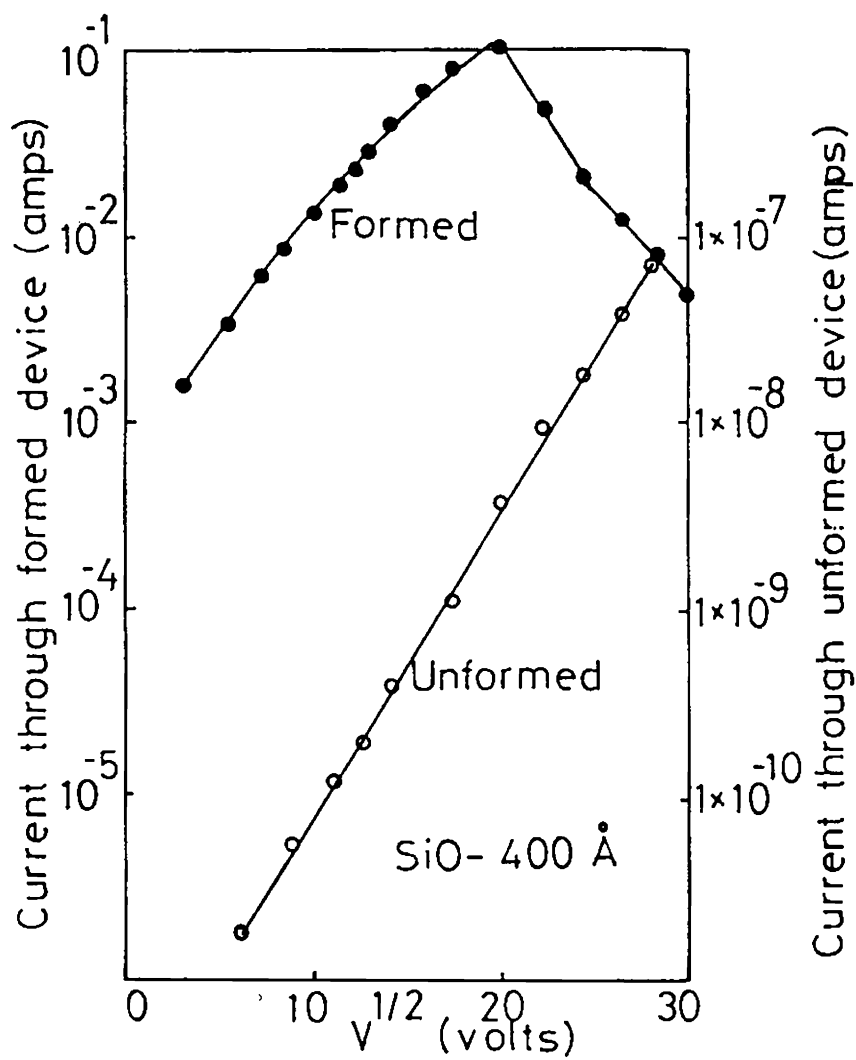
Fig.1.02   The current-voltage characteristic of unformed
           and formed sample $(I$ vs. $V^{\frac{1}{2}})$ illustrating the
           large change in conductivity that occurs due
           to 'forming process'.

Forming is found to depend on several factors like ambient atmosphere, thickness of the film, temperature, electrodes and the applied voltage. The mechanism of forming is explained in terms of ion injection by Verderber and Simmons [2]. It is also explained as due to the ionisation of the impurity centres resulting in the formation of impurity bands. This facilitates charges to tunnel between localised states and contribute to higher conductivity. A detailed review of forming and conduction is given by Ray and Hogarth [29].

## 1.30 MOTT TRANSITION

Any insulator metal transition is termed as 'Mott transition [30]. The switching in insulators can be closely related to Mott transition, as is evident from the investigations reported. In 1935 Gudden [31] and Schottky saw drastically altered kind of conduction in heavily doped materials. Mott predicted that abrupt increase in conductivity would take place by the overlapping of wave functions of the donor metal ions on one another when the density achieves certain value. A sudden shift to a quasi metallic conduction state occurs. Mc Irvine [32] gave an empirical relation for the critical concentration of doping as

$$N_c = (2.2 \ A_h)^{-3} \ \exp \ (1-\epsilon) \ donor/cm^3$$

$$= 1.6 \times 10^{24} \ \exp \ (1-\epsilon) \ donor/cm^3 \qquad (1.01)$$

where $\epsilon$ is the static dielectric constant and $A_h$ the Bohr radius. This has been verified for $Mg_2Sn$, NiO and SiC [32].

The Mott transition is very evident in antimony tri selenide crystals. When antimony is added to this crystal, the resistivity drops very abruptly as in Fig.1.03. When the stoichiometric proportion of $Sb_2Se_3$ exceeds on the antimony side, the temperature coefficient of resistance becomes positive showing the metallic type of conduction.

When the close isomorph $Sb_2S_3$ crystal containing about one per cent excess of antimony is examined by Gildart [33] by applying a field of 1000 V/cm, a bistable switching is observed eventhough a 'Mott transition' could not be seen. The initial high resistance state is attained by heating to about 200°C or when the sample is heated internally by passing a current pulse. They found that this process can be repeated. The switching is found to be due to a filamentary path. This switching is explained in terms of the overlapping of wave functions of two closely spaced antimony atoms in the fila- mental path. The internal heating by the current pulse rearranges the atoms so that no overlapping of wave functions is present. It is the excess of antimony atoms present in the crystal that causes this behaviour. It is possible that the amorphous structure is more prone to overlapping of wave
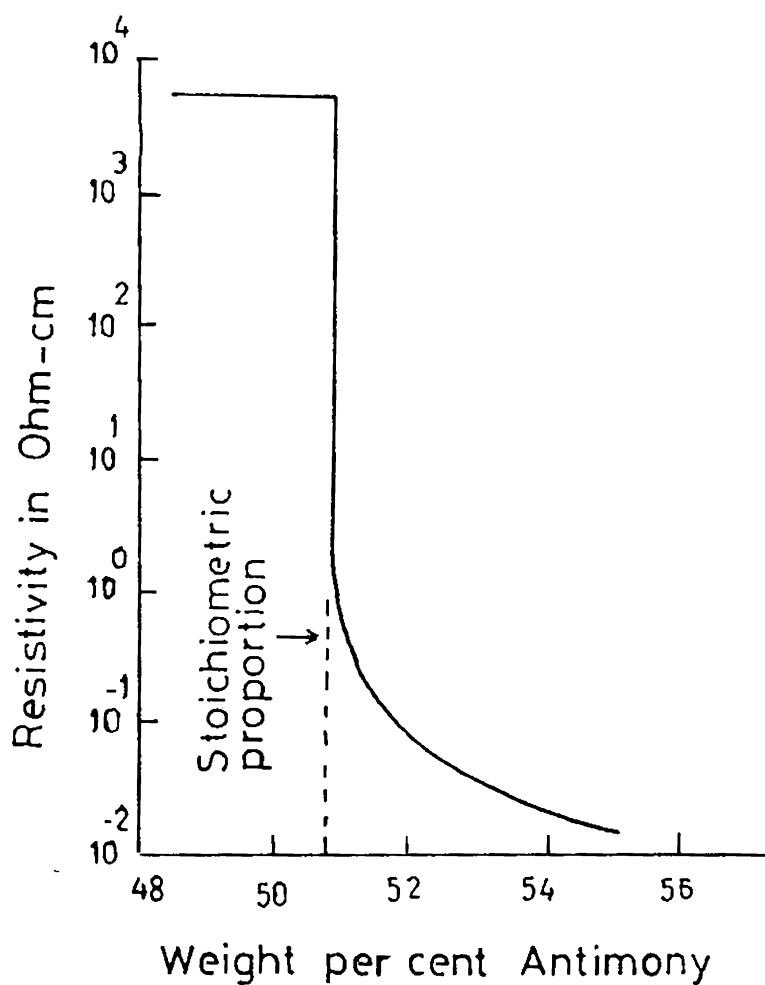
Fig.1.03 Resistivity of $Sb_2Se_3$ crystal as a function of weight per cent of Sb added to $Sb_2Se_3$.

functions. Likewise, impurities could play a major role in the switching mechanism. The high conductivity in metal containing organometallic polymers [34,35] may be a consequence of the overlapping of the wave functions.

## 1.40 CONFIGURATION USED FOR SWITCHING INVESTIGATIONS

The configurations for switching studies could be different according to the type of investigation. Ovshinsky [36] had taken a patent covering a number of configurations for the investigations on switching. The most commonly used configurations are: (Fig.1.04)

1. The point contact

2. The planar structure and

3. The sandwich structure.

The point contact has the advantage of probing different points of the film and in this configuration the effect of capacitance will be minimum. Using the planar structure, it is possible to directly observe the film through a microscope for any visible change of the specimen. Very small planar structure films could be obtained using very fine wire masks or by photolithography. The most common configuration is the sandwich structure which is the metal insulator metal (MIM) structure.
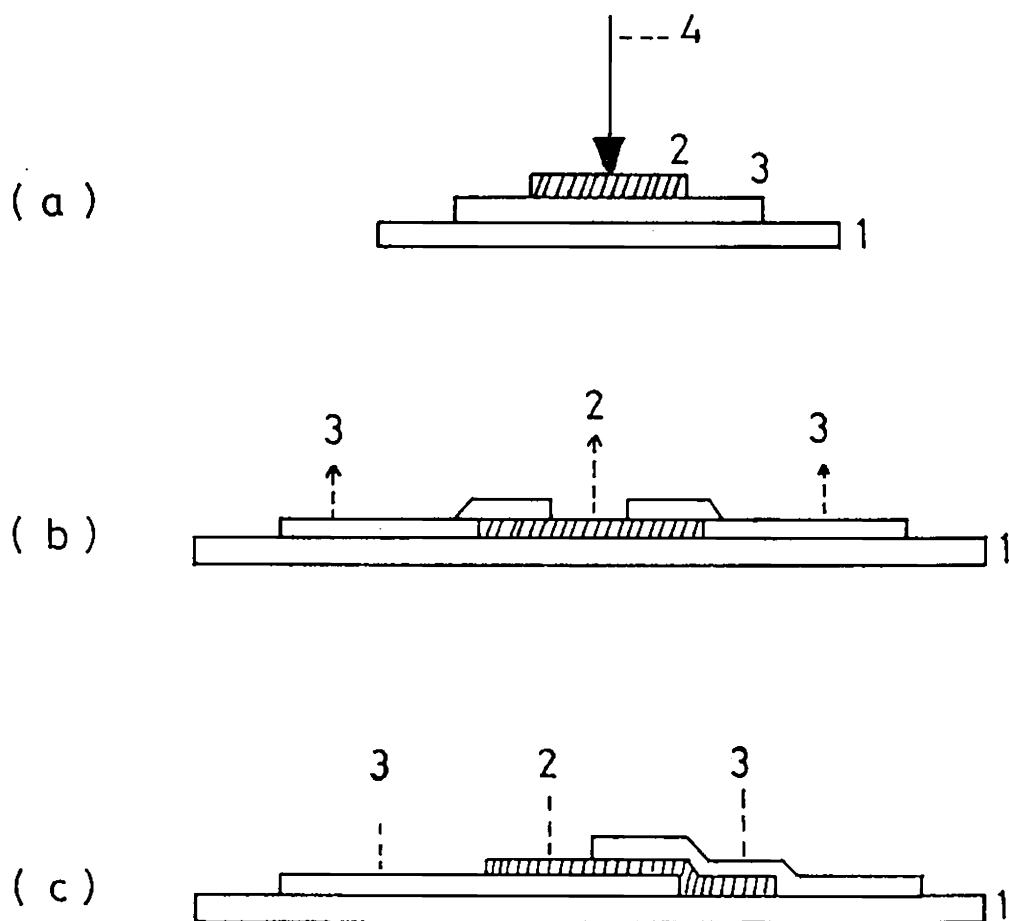
Fig.1.04  Schematic diagram of common configurations
used for switching investigations

(a) point contact, (b) planar and (c) sandwich

1—substrate,  2—specimen film,  3—metal electrodes
4—point contact.

## 1.50 SWITCHING AND ALLIED PHENOMENA

Switching is a nonlinear phenomenon which occurs at high fields (greater than $10^5$ V/cm). Under these fields, most of the materials undergo threshold, or memory switching or dielectric break down. Certain phenomena like current controlled negative resistance and voltage controlled negative resistance are associated with switching. Following are the important allied phenomena illustrated in Fig.1.05.

### 1.51 The switching device

As the voltage exceeds the threshold voltage $(V_{th})$ the device switches. However, this device has no stable operating point between the high impedance OFF state and the low impedance ON state [37]. When the current is lowered below the holding current, the device goes back to the high impedance OFF state. This is the typical threshold switching and the characteristic is symmetric with the polarities (Fig.1.05 a).

### 1.52 Memory switching device

This device shows the memory effect. The switching takes place at a threshold voltage. The conductive ON state is retained even after the removal of the applied bias [38,39]. There is no stable operating point between the OFF and the ON states (Fig.1.05 b).

1.53  Negative resistance device

This device has an I-V characteristic which is retraceable except when there is hysteresis for a rapid change of current (Fig.1.05 c). Thermistor is an example of this device. By using a small load resistor switching can be effected.

1.54  Negative resistance device with memory

This device has two stable states. A conductive state is formed after the negative resistance region [40,41] at higher current (Fig.1.05 d). The initial state is attained above certain high current. This is found in oxides. In some cases, polar behaviour is also observed.

1.55  Voltage controlled negative resistance device

This device is described by Simmons and Verderber [2]. Such a phenomenon is found in wide band gap materials like $SiO_x$ which undergo a forming process under certain applied voltages. When the voltage is reduced slowly the I-V is retraced. However, if changed rapidly the high resistance would remain. The low resistance can be attained by using a pulse at higher voltage. A unique feature is that the device is capable of existing in different memory [42,43] states depending on the choice of point from which the voltage is reduced (Fig.1.05 e). This is associated with electronic trapping.
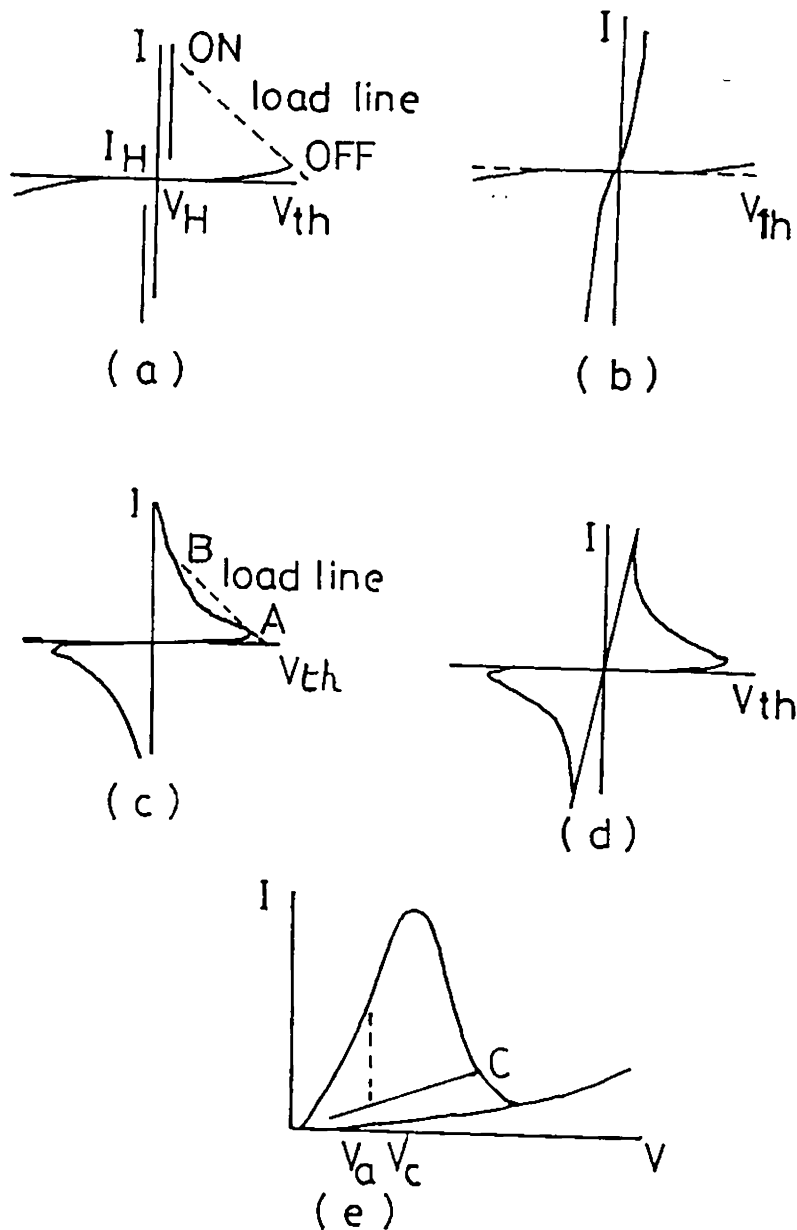
Fig.1.05   Schematic illustrations of various allied phenomena
of switching (a) the switching device, $V_{th}$- the
threshold voltage, $I_H$ - the minimum holding current
$V_H$ - the holding voltage. (b) memory switching device.
(c) negative resistance device. (d) negative resist-
ance device with memory. (e) voltage controlled
negative resistance device with memory, $V_c$ - the reset
pulse voltage, $V_c$ - the critical voltage above which
negative resistance begins, c - the choice point from
which voltage is reduced.

## 1.60 THE I-V CHARACTERISTICS

A typical I-V characteristic is as shown in Fig.1.06. The switching event develops in four sequential steps. Initially the current through the specimen is very small. As the applied bias reaches a particular threshold voltage $V_{th}$, a stage of instability and current run away occurs and abruptly the current reaches a high value. The voltage collapses with the discharge of electrostatic energy stored in the specimen. A new low voltage ('V' ON) high conducting steady state is reached. The ON state current $I_{ON}$ is limited by the external circuit resistance. In the case of threshold switching, there is a minimum holding current $I_{MH}$ below which the specimen resistance goes high. Once switching has commenced, it proceeds very rapidly with a switching time $t_s < 10^{-6}$ seconds to the conducting branch of the I-V characteristics. This is again limited by the shunt capacitance and the series inductance of the leads. The OFF state resistance is of the order of $10^5$ to $10^7$ ohms at 300 K. In the conducting ON state the resistance will be 10 to 1000 ohms and the voltage drop will be typically 1 to 3 volts and is nearly independent of current. The principal difference between threshold and memory device is that in the threshold switch a holding current $I_{MH}$ typically between 0.1 and 0.5 milliamp. is observed below which the ON state cannot be maintained and the device returns to the OFF state.
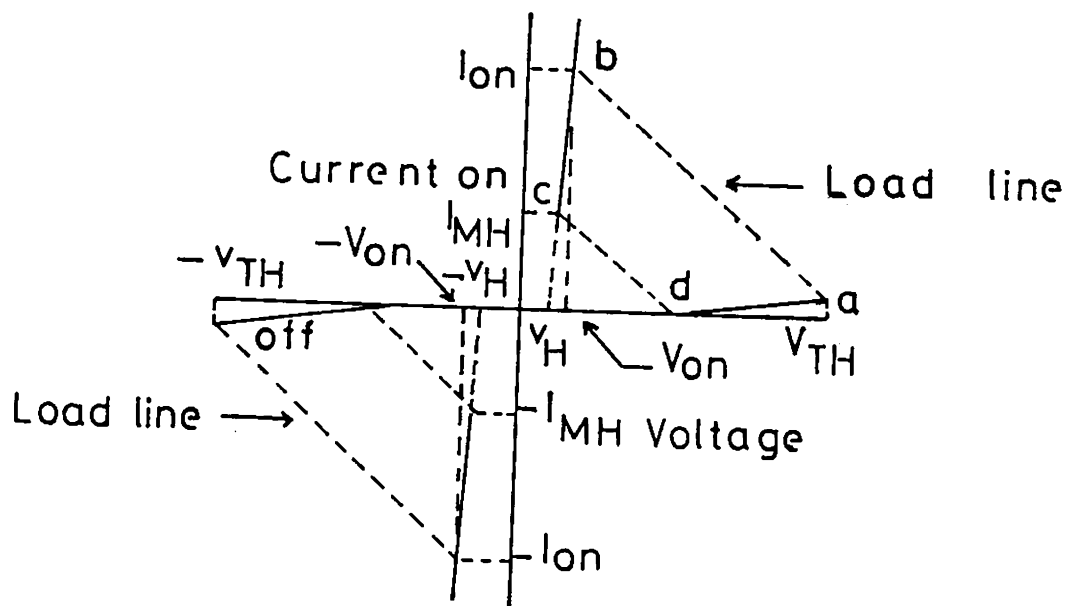
Fig.1.06  Typical switching characteristic.
$V_{th}$ - the threshold voltage, $V_H$ - the holding voltage, $I_{MH}$- the minimum holding current, $I_{on}$- the on state current, $V_{on}$- the on state voltage.

## 1.70   IMPORTANT PARAMETERS OF SWITCHING

### 1.71   Threshold voltage $V_{th}$

The threshold voltage is the voltage that is just sufficient to switch ON the device to the conducting state from the non-conducting state. $V_{th}$ is found to depend on the material, the method of preparation, the electrodes used the ambient atmosphere, the temperature, frequency of the voltage, contact thrust and the substrate used. With these parameters $V_{th}$ is found to vary from 1-1000 volts. $V_{th}$ is found almost linear upto a few micron thickness of the material and increases in general with decrease of temperature. In some cases like $Te_{81}Ge_{15}Sb_2S_2$, $V_{th}$ versus thickness curve extrapolates to a finite voltage intercept for zero thickness. This is true when the voltage is slowly varied, and is attributed to non-uniform thermal effects [44]. Walsh et al. [45] have pointed out that $V_{th}$ becomes zero close to the glass transition temperature $T_g$. But this is not generally true. Haberland et al. [46] studied the sinusoidal frequency dependence of $V_{th}$. At higher frequencies $V_{th}$ is found to drop. This is due to finite recovery time of the device.

When the applied bias is close to $V_{th}$, one observes a statistical variation of several per cent of $V_{th}$. This variation can be minimised by applying 20 per cent over voltage.

The effect of contact thrust on switching has been investigated by Henisch and Mayers [47]. The threshold voltage and the zero voltage resistance $R_o$ are found to decrease by the increase of the contact thrust. This is again reported by Mayers [48] in evaporated polyacrylonitrile films. Hemamalini et al. [49] reported pressure dependent switching in charge transfer complex, O-Tolidine-iodine. $V_{th}$ is found to decrease with the applied pressure. The effect of different substrates on $V_{th}$ has also been investigated by Henisch and Mayers [47] and subsequently by Ramke et al. [50]. Walsh et al. [45] could obtain a relation for $V_{th}$ in terms of temperature and pressure variations. The plot between switching temperature and the switching pressure is as given in Fig.1.07. The region above the line represents the conductive ON state and the region below the line the non-conductive OFF state. These measurements are for a finite applied field. This shows the existance of a thermodynamic phase boundary between the ON and OFF states. Henisch et al. [51] showed that it is possible to initiate switching by light pulse directed to a speciman suitably biased. This facilitates opto electronic application.

## 1.72  Time response to a  voltage pulse and delay time

The time response to an voltage pulse $V_p$ greater than $V_{th}$ is as shown in Fig.1.08 for threshold and memory devices. When a voltage pulse $V_p$ exceeding the threshold
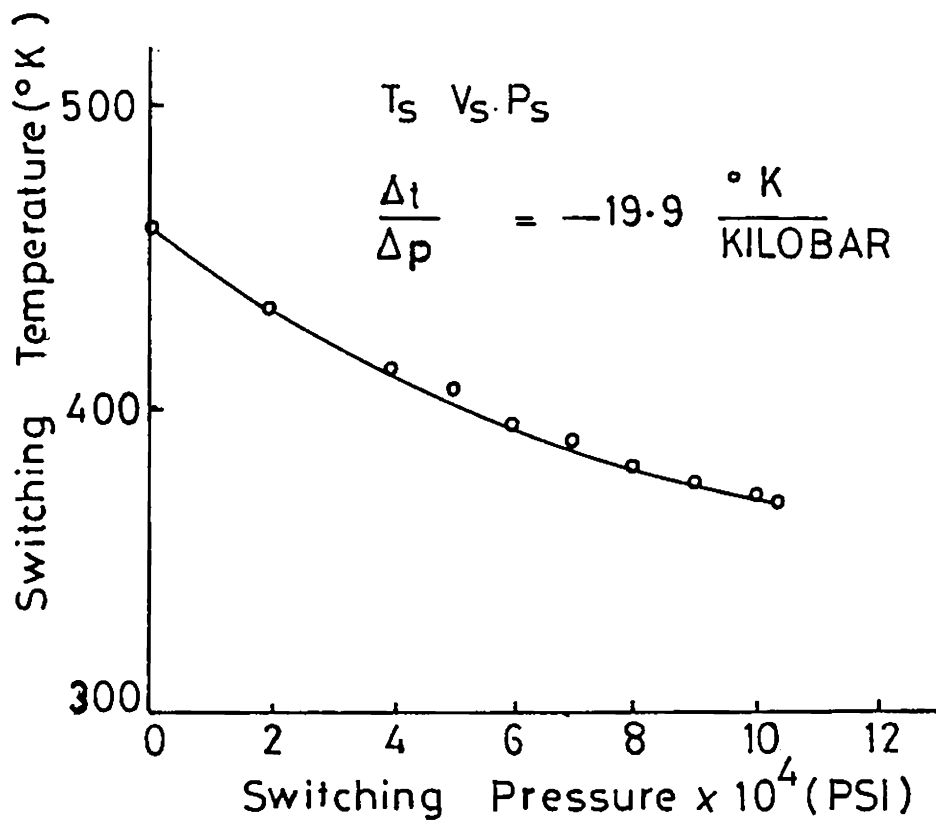
Fig.1.07. The derived dependence of switching temperature on switching pressure. The slope $\Delta t/\Delta p$ is at zero pressure, indicated.
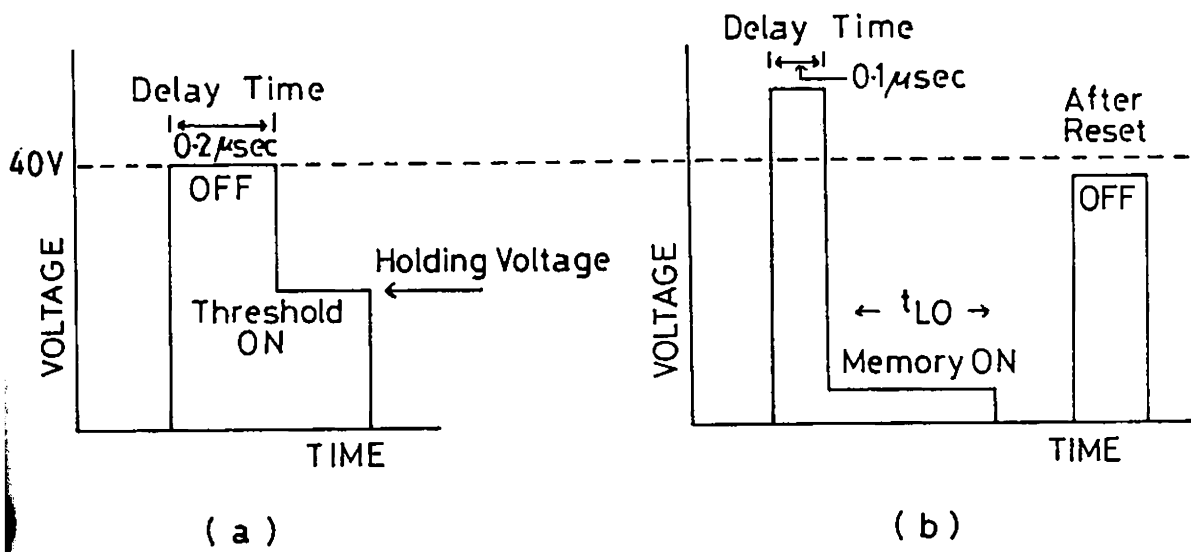
Fig.1.08. Time response of a switch to an voltage pulse $V_p$ greater than $V_{th}$ (a) for a threshold switch, (b) for a memory switch, '$t_{LO}$' is the lock on time for memory to take place.

voltage $V_{th}$ is applied, switching to the ON state occurs after a delay time $t_D$. In the memory switching device there is a lock on time $t_{Lo}$ during which the memory action takes place. If the voltage pulse is removed below $t_{Lo}$ no memory would take place, instead there will be a threshold behaviour even for a memory switching device. The memory is erased by using a reset pulse of higher current. In order to avoid the thermal problems, the parallel capacitance of the circuit and device must be kept a minimum so that the discharge heat spike is a minimum.

The delay time $t_D$ measures the interval between the application of a voltage pulse $V_p$ and the initiation of switching process. The delay time $t_D$ decreases rapidly as $V_p$ is increased beyond $V_{th}$ and for $V_p$ greater than 1.2 $V_{th}$, it follows the relation [3].

$$t_D = t_{Do} \exp (-\alpha V_p) \qquad (1.02)$$

The prefactor $t_{Do}$ decreases with increasing ambient temperature and decreasing electrode separation. The typical delay time is in the range $10^{-6}$ to $10^{-10}$ seconds. Lee et al. [52] observed a statistical fluctuation of $10^{-3}$ $t_D$ even at larger over voltages. The effect of opposite polarity of

$V_p$ on delay time was studied by Shanks [53] on the belief

that charge carrier injection plays a major role in the

switching process and in determining $t_D$. They found $t_D$ to

remain same eventhough $V_p$ was reversed during the delay period.

Henisch and Pryor [54] in their experiment found that even-

though the total delay is lengthened to 0.9 $\mathcal{U}$ seconds from

0.6 $\mathcal{U}$ seconds the delay of the positive pulse is somewhat

shortened to about 0.4 $\mathcal{U}$ seconds by the presence of negative

pulse. Also one observes that a non-switching 'A' pulse

applied would shorten the delay time for a switching 'B'

pulse more than when opposite polarity is used. This indi-

cates that only a part of the opposite polarity is causing

the delay in switching. This small delay due to the opposite

pulse is explained as due to the opposite pulse is explained

as due to the space charges at the electrodes.

Haberland [55] explored the possibility that the

switching is due to the charge accumulation during the delay

time $t_D$ and this is true at least for the threshold switches.

The charge storage depends on the time and ambient temperature.

The minimum charge needed for switching is obtained from  a

plot of accumulated charge versus delay time. More insight is

possible by the life time measurements of charges in the ON

state of a film. In thermal model delay time of the order of

seconds and lock on time of the order of minutes are observed. The delay time and the variation of specimen voltage and current of a switching device under pulse excitation is as shown in Fig.1.09.

### 1.73 ON state of a threshold switch

The ON state of a threshold switch is studied extensively by Pryor et al. [56], Henisch et al. [54,47] and Mayers [48]. After switching to the ON state by the application of a threshold voltage, the ON state would be generally seen only for a short time. This state vanishes and the high impedance state attains after a time interval $t_m$ of the order of a few seconds. The ON state can be maintained by interrupting the ON state within the maximum recovery time $t_m$ by pulses of short amplitude and duration (transient pulses) as shown in Fig.1.10. After the $t_m$ a full threshold voltage is to be applied to bring back the ON state. The ON state condition prevalent due to the transient pulses is known as the transient ON state condition (TONC) [56]. In this state, the transient current is exceedingly small and the state is termed as the 'blocked ON' state. If the polarity of the transient pulse is reversed, no transition to an OFF state is caused but the ON state is readily prevailed in the blocked ON state. The transient ON state readily joins the ON state above $I_{MH}$, the minimum holding current. The ON state
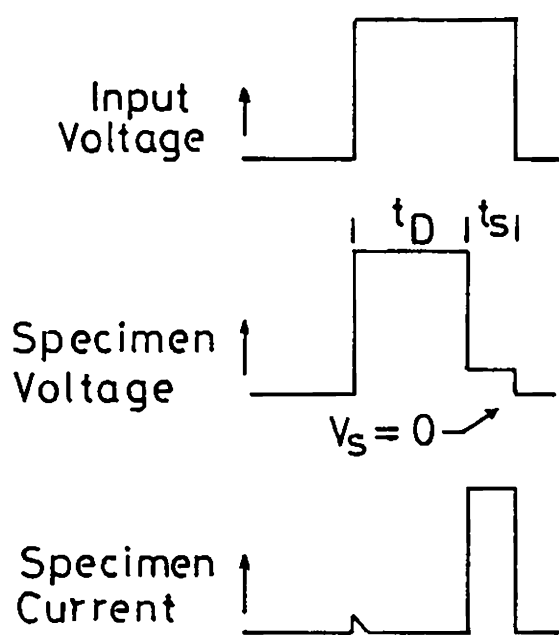
Fig.1.09. Illustration of specimen voltage and
current under pulse voltage switching,
$t_D$ - delay time, $t_S$ - the switching
time.
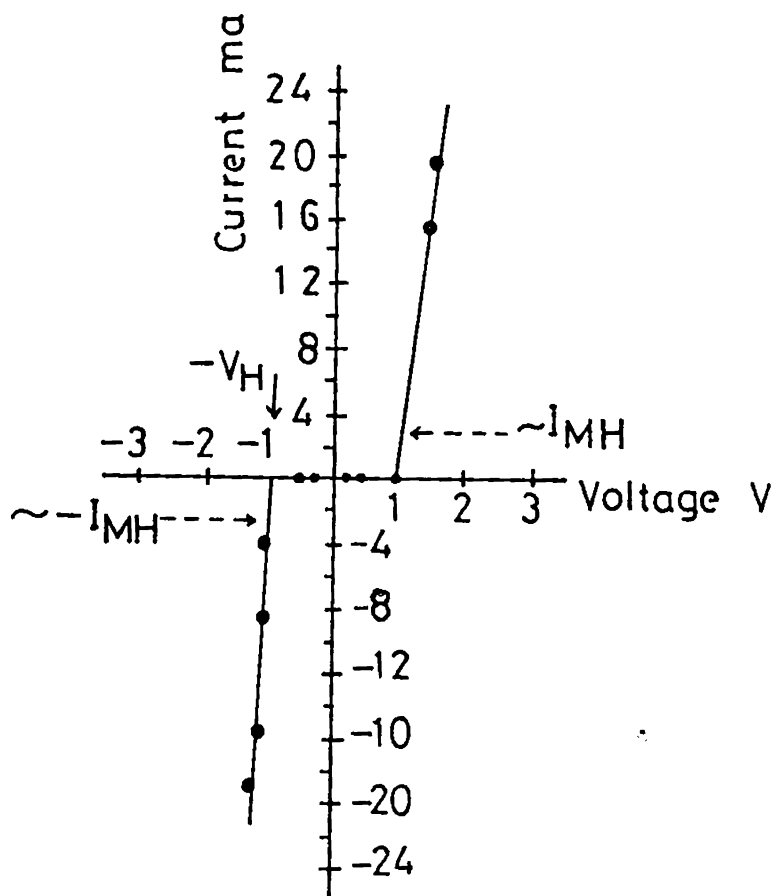
Fig.1.10. Schematic illustration of the transient
ON state condition (TONC) of a threshold
switch. The region of characteristic on
the voltage axis with exceedingly small
current represent the TONC. $I_{MH}$ - the
minimum holding current and $V_H$ - the
holding voltage.

of threshold switch is analysed using single pulse method
or double pulse method described by Pryor et al. [56],
Mayers [48] and Fritzche [57].

## 1.80 SWITCHING MECHANISMS

The switching mechanisms, both in threshold and
memory switching are much diverse in nature and are very
different from dielectric breakdown in which the film is
destroyed. The non-destructive property of the material under
high power conditions is important in this study. The under-
standing of the physical aspects involved in switching
necessitate further investigations in this field. The
conduction mechanisms before forming and switching are more
clear. This include ohmic, ionic, space charge limited,
tunnelling, Schottky emission and Poole-Frenkel conduction.
These conduction mechanisms are studied and reviewed by many
authors and discussed subsequently. The regenerative process
of switching is related to one or combination of these
conduction mechanisms. The mechanism of switching differs
from material to material and are mainly brought under
(1) Thermal    (2) Electrothermal and    (3) Electronic.

## 1.81 Thermal mechanism

In thermal model the resistance of the material
rapidly decreases on increasing the temperature. In this,

Joule heating raises the temperature inside the material and this allows more current to flow as in a thermistor. This again raises the Joule heating until a stationary state is attained in a plateau region, when the heat conducted away is equal to the heat generated in the current path. The phenomenon is possible in materials with large negative temperature coefficient of resistance and is found in semi-conductors. Thermal switching and break down were investigated by Fock [58] and Boer [59]. When the electrodes are perfect heat sinks, negative resistance is not observed and hence no switching occurs. This was proved by Kaplan [60] and also by Alder and Keyes [61].

## 1.82 Electro thermal mechanism

Electro thermal mechanism is common in many switching materials. The earlier investigations are made by Kroll and Cohen [62]. The switching is effected by the formation of conducting channels across the electrodes. This channel conduction is found commonly in chalcogenide glasses [63] and is observed using a microscope. They observed channels of 1 to 10 micron diameter in $AS_2SeTe_2$ glass. Stocker [64] demonstrated molten channel formation in $Ge_{12}As_{19}Te_{69}$ glass. Hickmott [65] observed channel conduction in $Nb-Nb_2O_5$-Au devices. The rapid growth of the channels ($10^{-10}$ sec.) and

a current of 5000 to 1,00,000 amp./cm$^2$ through the channels
are quite astonishing and is not supported by ordinary
materials without strong heating effects. A major effect that
can explain high current densities is the dangling bond wave
function overlap near zero activation energy or complete
degeneracy.

Matare 66 put up a quasi long range order due to
the field ordering by rotation of sufficient number of free
bonds to form a channel. This rotation of free bonds yield
channels to form in the grain boundaries. The overlap of
wave functions in Mott 30 transition is modified to account
the field ordering and grain boundary conduction in which
impurities are absent. A field ordering model in the case of
Vanadium Pentoxide is also described. The model is as shown
in Fig.1.11.

Vogel 67 showed that the capacitance of the
switching sample decreases to 2 PF before the channel formation
and attains negative values (-3 to -4 PF) after the channel
formation. This negative capacitance shows the presence of
the conducting channels. At the same time the inductance
assumes positive values.

Fig.1.11. Proposed scheme of charge transfer
through vanadium oxide glass due to
field ordering.-O - Oxygen,
-•-Vanadium 4+, -◎-Vanadium 5+

The conducting channel formation is effected in different ways. This can be due to a phase change channel formation as in chalcogenide glasses. In Tellurium containing alloys the formation of tellurium crystals through phase separation creates channels [62]. In the case of certain carbon containing polymer materials such as styrene, benzene and acetylene, pyrolysis and formation of carbon filaments is the basis for channels formation [68].

In $Ag_2Se/Se/metal$ structure [69] and silver photo doped $As_2S_2$ [70], switching takes place by the formation of channels due to silver ion migration. In these cases, polarity dependent behaviour is also seen. Swaitek [71] investigated switching in P-quarter phenyl layers which is an organic material. Here also conducting channel formation is explained as the switching mechanism.

In electro thermal mechanism the threshold voltage is found to vary as a function of temperature as shown in Fig.1.12. The threshold is also an increasing function of film thickness. Pender and Fleming [68] observed in polystyrene films, spots of filament formation after the forming process and switching. The filament size is about 10-100 micrometre in diameter. The switching is erratic and finite for certain number of cycles in these films. However, the number of events is as high as $10^6$ cycles. The switching is explained by the formation of a number of carbon filaments.
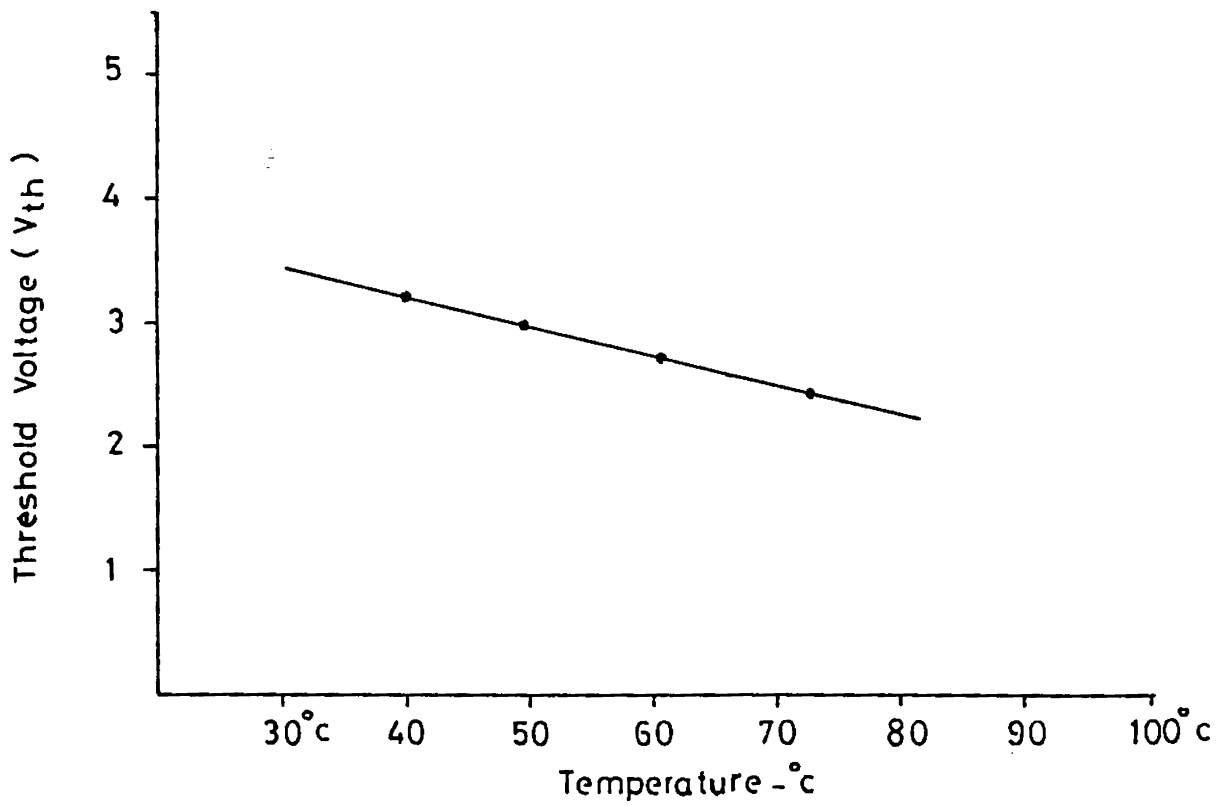
Fig.1.12. Variation of threshold voltage with specimen
temperature in electrothermal model for
switching.

This formation of conducting channels across the electrodes gives rise to memory switching. The current would increase as more and more filaments are formed. The erratic switching behaviour is due to the random number of filaments involved in each switching cycle. This poly filamentary model is first proposed by Dearnaley et al. [72] and then by Wood Cock [73]. The model of switching is as illustrated in Fig.1.13. Segui et al [74] studied plasma polymerised polystyrene. They used tungsten electrodes so that the contribution of electrodes by melting and forming metal bridge is avoided. They have also observed switching.

In this model, the current is found to be independent of the area of the film. This demonstrates the filamentary nature of the current. The transition from ON state to OFF state is performed by the application of a suitable current pulse which reptures the filament. They equated the heat energy supplied to the film in ON state and the energy dissipated in the film as follows:

$V_1$ is the voltage delivered by the generator, $V_2$ is the voltage across the resistance connected in series with the film so that $(V_1 - V_2)$ is the voltage across the structure.

Carbon Rich Area  Formed Conductive
Ruptured Filament  Filament

Upper
Electrode

Polymer
Film

Substrate

Lower
Electrode
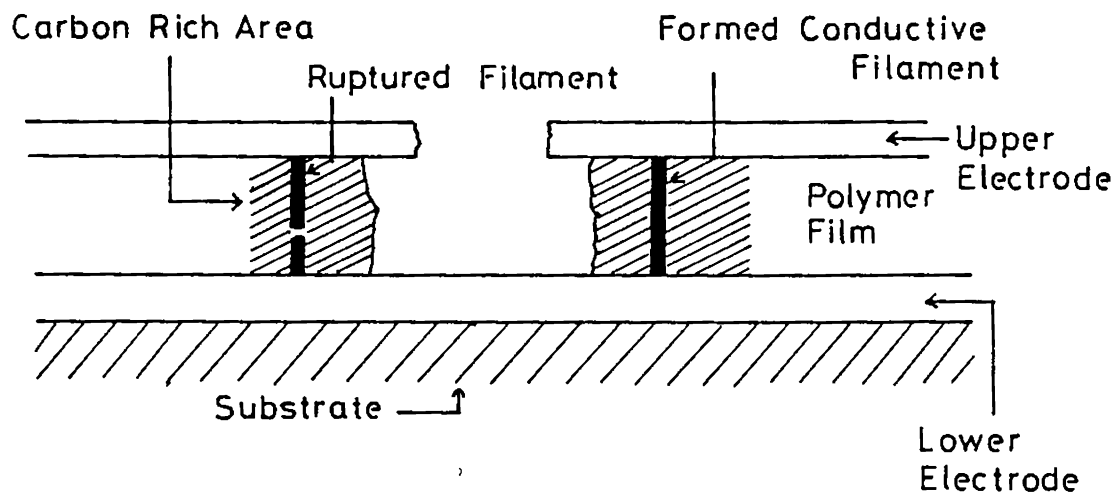
Fig.1.13. Proposed electrothermal model for switching
with channel formation.

The time interval taken is $t_D$ and the current through the structure is I. So the energy supplied to the structure is

$$E = (V_1 - V_2) I \, t_D \qquad . \qquad (1.03)$$

This is the regeneration energy supplied to the film to revert from the ON state to the OFF state. This energy is found to be higher as the resistance of the film is lower due to the size and higher number of filaments as shown in Fig.1.14. If we consider a single effective channel, then the resistance of the structure is connected to the channel volume by the relation 74 .

$$V = \frac{\rho L^2}{R_m - R_o} \qquad (1.04)$$

where V is the channel volume, $\rho$ is its resistivity, L is its length $R_m$ is the measured resistance and $R_o$ is part of $R_m$ due to the contact.

Equation (1.04) can be rewritten as

$$V = \frac{\rho L^2}{1 - R_o (1/R_m)} \frac{1}{R_m} \qquad (1.05)$$

If we assume that all of energy is dissipated in the channel, then we can write the equilibrium equation as
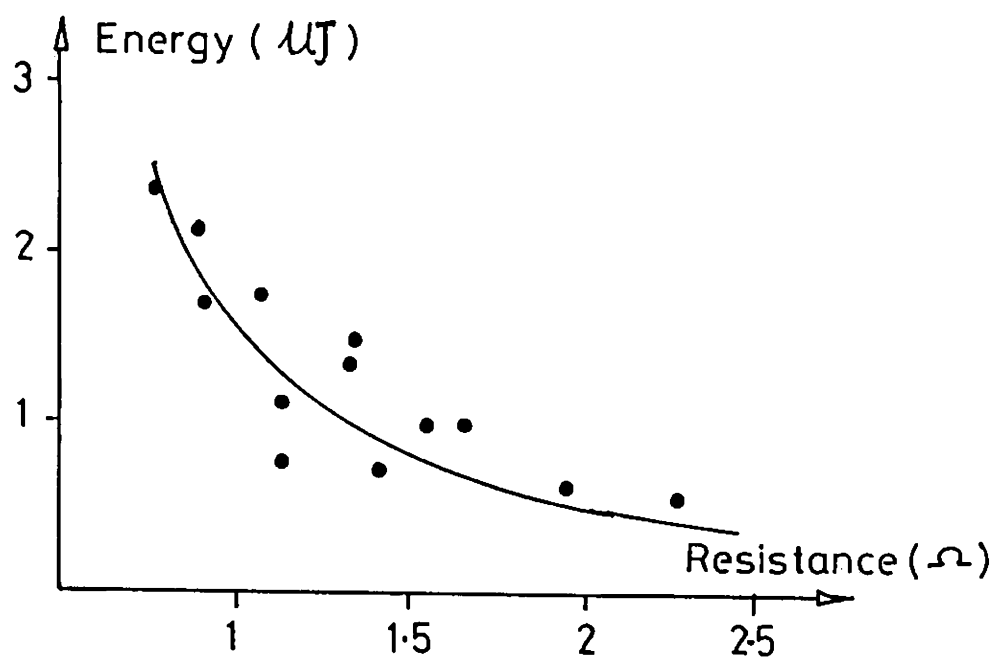
Fig.1.14. The regeneration energy needed to revert from the ON state to the OFF state versus channel resistance. (µJ)- microjoules.

$$C_v (T_m - T_o) \, V \mu' + L_v \mu' = (V_1 - V_2) \, I \, t_D \qquad (1.06)$$

where $C_v$ is the specific heat, $T_m$ is the maximum temperature reached by the channel that is the sublimation temperature for amorphous carbon. $\mu'$ is the specific mass of the material constituting the channel and $L_v$ is the latent heat of vaporisation. Substituting for V in equation (1.06), we get the relation between $1/R_m$ and $t_D$. From this plot of $1/R_m$ versus $t_D$ (Fig.1.15) we see that as the resistance is lowered delay time is increased as obtained theoretically and experimentally. Segui et al. [74] have also performed gas phase chromatography. They observed the presence of hydrogen generated from the pyrolysis of the polymer due to the switching. This also supports the carbon channel formation in the switching event. Matare [66] and also Ray and Hogarth [29] have given a detailed account of forming and channel conduction.

Many of the observed phenomena like threshold behaviour, electron emission, radiation emission, ON state resistance variation and the ON state resistance oscillation in certain switching materials are not successfully explained by the filamentary model of switching. The electronic mechanism of switching would explain these phenomena in greater depth.
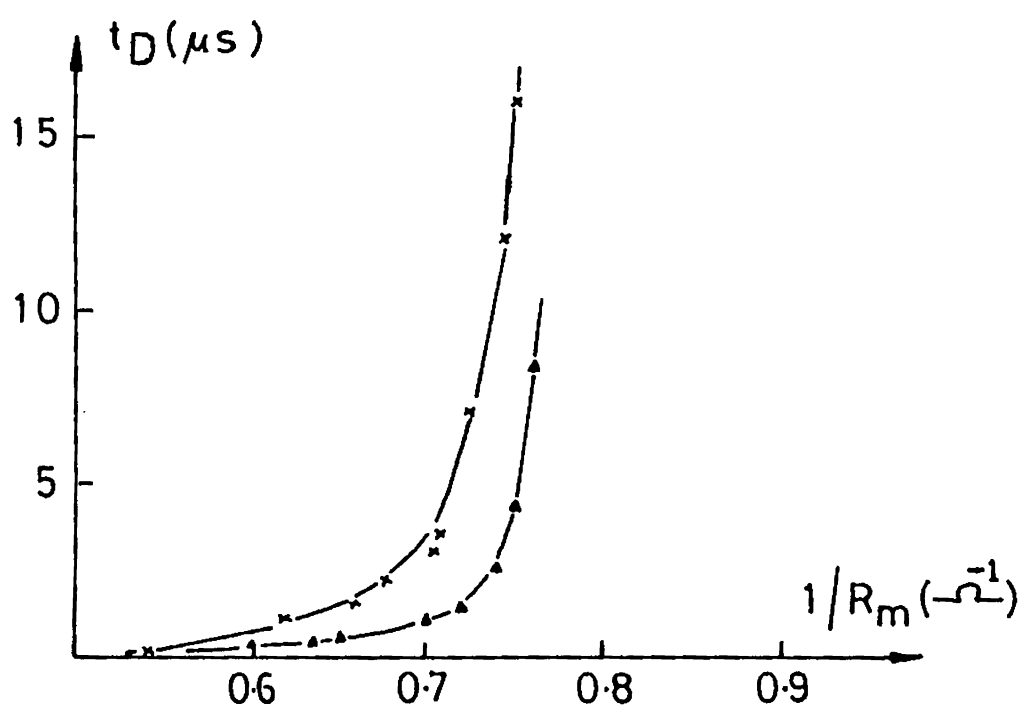
Fig.1.15. Delay time $t_D$ versus reciprocal of the channel resistance $(1/R_m)$.

## 1.83 Electronic switching mechanism

The most reliable mechanism to explain stable and reproducible switching is the electronic mechanism. Both memory and threshold switching are satisfactorily explained by this mechanism. Threshold switching is perhaps the best example for an electronic switching. The large field enhancement and switching could be explained due to the electronic processes such as trap limited space charge saturation, impact ionisation followed by avalanche, double injection and high field tunneling. The electronic switching mechanism is capable of explaining many of the phenomena like threshold behaviour in threshold switches and memory switches for switching time less than the lock on time [57], the high speed switching in less than $10^{-10}$ seconds and the frequency dependent behaviour [75]. All these phenomena support the electronic nature of switching. Crottoru and Gunbaum [15] have reported polarity dependent electronic switching in a-Si/$In_2O_5$-$SnO_2$ junctions. Eventhough electronic switching is the mechanism in these cases, the current takes a channel path and Joule heating is common with subsequent thermal effects.

Mott [76,77] discussed in detail how space charges can be maintained in the ON state of a threshold switch.

Most of the voltage drops at one or both electrodes. This distortion of field is due to the space charge adjacent to the electrodes and the centre region is free of space charge. Mott envisages a process in which the tunneling carriers move much faster than the carriers in the bands. And as a result, the space charge near cathode is positive and near anode negative. The work of Pryor and Henisch [56] has established that the currents and voltages can be reversed with in nano seconds. This supports that the mobile charges, or shallow traps take part in the space charge formation. Moreover, the ON state could not be frozen in liquid helium temperatures [78,79]. Hindley [80] and Mott [77] estimated the critical field beyond which the mobile carriers gain energy from the field at a rate faster than they lose it via phonon emission. Beyond this critical field, avalanche occurs which leads to the formation of a conducting plasma which can be sustained by the field near the electrodes. The critical field is given as

$$e\mu F^2 = \hbar w_p^2 \tag{1.07}$$

where $\hbar w_p^2$ is the phonon energy involved and is 0.03 ev and mobility $\mu$ is of the order of 3 $cm^2/V$ sec. Then the critical field F is of the order of $3 \times 10^5$ V/cm. This field

has the same value as for the threshold switching. This relation shows a temperature independent behaviour at low temperatures. But at high temperatures, this heating effect is larger and causes the field to increase near the electrodes [81]. According to Mott, the mobility of carriers always increases with energy above the mobility edge so that an avalanche should be produced. In this case the carriers gain energy than the rate of loss to the phonons.

According to Fritzsche and Ovshinsky [82] field enhanced hopping of carriers from occupied states below to empty states above the fermi level $E_F$ causes a non-equilibrium distribution of carriers which can be described by splitting of $E_F$ into two quasi fermi levels as shown in Fig.1.16. This increases the conductance. The excess current cannot be replenished by the electrodes and hence a positive space charge at the cathode and a negative space charge at the anode are formed. Tunnel injection occurs and replenishes the excess charge needed. The bulk conductance is high and a potential drop occurs at the electrodes.

Henisch, Fagen and Ovshinsky [83] in their model suggests double injection as the primary cause for switching. In this a negative space charge near cathode and a positive space charge near anode build up due to the trapping of
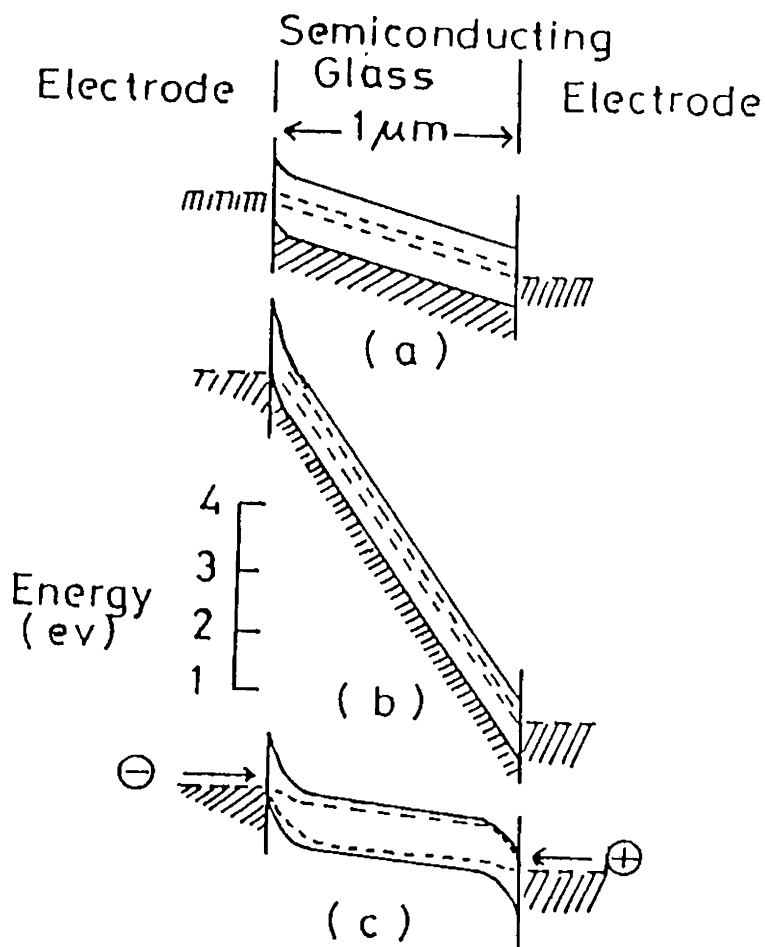
Fig.1.16. Sketch of potential profile (a) & (b)
before switching with applied fields
of roughly $10^4$ and $6x10^4$ V/cm respecti-
vely. The switching field is about
$5x10^5$ V/cm. (c) the potential profile
after switching. The dashed line repre-
sent the quasi Fermi levels for electrons
and holes respectively. The arrows indi-
cate the injection.

injected charge carriers. In this model, the cathode is ohmic to the electrons and anode ohmic to the holes [84]. This situation increases the carrier concentration. The two space charges act as virtual electrodes. Switching occurs by the overlap of these space charges resulting in the filling of holes and electron traps. The field collapses with the space charge spreading to the bulk of the specimen.

Van Roos Broeek [85] assumed that the recombination time $\tau_o$ is much shorter than the dielectric relaxation time $\left( \tau_{rel} = \frac{\varepsilon \varepsilon_o}{\sigma} \right)$ and the minority carrier injection does not split the fermi level to quasi levels but shifts near to the conduction band. The switching is then controlled by the recombination front. In this case, the space charge spreads to a depth of $\mu_D F_m \tau_{rel}$, where $\mu_D$ and $F_m$ are the drift mobility and maximum field which occurs at the end of the space charge. The thickness of the film is to be small for switching controlled by recombination front to take place.

The maintenance of the ON state with excess charge is thus the cause of the electronic switching. The role of space charges at the electrodes and the geometry of the specimen are very evident in electronic switching. This would

in turn show a poor dependence of $V_{th}$ on the film thickness and temperature which is actually observed. If the injection drops below a certain value, the recombination wins and the specimen returns to the OFF state. This explains the minimum holding current for the sustenance of the ON state in a threshold switch. This situation is analogues to the charge density variation in the base region of a switching transitor in the OFF and in the ON states described earlier. Athwal et al. 86 have studied the switching and the associated electron emission in their investigations. A resistance oscillation behaviour is reported by Weinreb [87] and Pender et al. [68]. More details are not reported about the resistance oscillation. However these oscillations can be related to the space charges.

Stocker et al. [88] and Kolomiets et al. [89] observed radiation emission along with threshold switching. This can only be accounted by an electronic phenomena. The emission can be due to spontaneous band gap emission or due to hole electron recombination. According to Vezzoli et al. [90] stimulated emission can also occur during the ON state of a threshold switch. In polymethyl methacrylate which is an insulating polymer [47] threshold switching is observed.

As the polymer is devoid of free carriers, the switching can only be due to the injected carriers and space charge formation. Henisch and Smith [91], showed both threshold and memory switching in polytyrene. In polymethylmethacrylate, polyethyl methacrylate and poly butyl methacrylate, threshold switching is reported by these investigators.

Electronic memory switching is found in many materials [9,92,93] of elemental origin, compounds, heterojunctions and polymer materials. Feldman and Moorjani [9] investigated switching in Silicon, Boron and Germanium. The memory in these materials is explained to be due to the ionisation across the band gap followed by the filling of traps. Memory switching is reported for organic films of p-quinqua phenyl [94], and for poly N-vinyl carbazole [94,95]. The memory is due to the ionisation of the traps present in these materials. The trap density and the critical switching field is related as [95].

$$V_{th} = \frac{e\ NL^2}{\varepsilon\varepsilon_o}$$

(1.08)

where N is the total density of trapping levels L the thickness of the sample, $\varepsilon$ the dielectric constant and $\varepsilon_o$ the dielectric permittivity of free space. The trap density can

be as high as $10^{22}/cm^3$ in amorphous materials. This very

high trap density together with charge storage capability

would facilitate memory switching in materials.

Switching in heterojunctions is due to the ionis-

ation in the interface region. This results in a high field

region and tunnelling takes place through the empty traps

transforming the high impedance region to a region of ohmic

contact. The major requirement for switching is a thin

semiconductor with sufficient trap density. This is true in

the case of ZnSe-GeAs, GaP-Ge, GaP-Si and ZnSe-Ge [12,38]

heterojunctions. Some other heterojunctions are ZnTe-Si [96]

and $SiO/In_2O_3$ [97] which are found to show memory switching.

Since the ionised traps in the bulk must remain empty with

time, inspite of the high electron density, it seems necessary

that they may be Coulombic repelling [98] sites. Doubly

negatively charged traps before ionisation and singly negatively

charged traps after ionisation would provide such a condition,

because a barrier is present to the electrons that prevents

refilling the traps immediately and eliminates the memory.

Such traps are common in II-VI compounds. The Zn vacancy is

of such a nature, since Zn is a double acceptor. The memory

is lost by recombination. This recombination may be governed

by critical conditions and needs further investigation to

reveal the effectiveness of memory and its erasal.

Some other switching mechanisms are also reported.
For example, in the case of polyanthracene [99] switching is
explained by polymer monomer conversion. Another novel
mechanism of switching is postulated by Hall et al. [100]
based on charge density wave depinning. This is a collective
mode of charge transport involving electron-phonon interaction.
Such conduction is possible in chain like incommensurate
systems such as tetracynoquino dimethane, potasium cynoplati-
nate and certain other charge transfer complexes. Frequency
and field dependent conductivity is the evidence for collective
charge transport mechanism.

## 1.90 POLYMERS AS SWITCHING MATERIALS AND THE SCOPE

Polymers are long chain molecules with high molecular
weight. They are formed from simpler molecules by covalent
bonding. Polymers may be formed from organic or inorganic
compounds. However, inorganic polymers are sparse. Only very
few of them are found like $(SN)_x$ [101] and recently reported
[102] photoresponsive paramagnetic polymers of titanium,
zirconium, niobium and tantalum rare earth metal alkoxides.
As they are rare earth compounds, these polymers are possible
candidates for super conducting polymers.

The field of polymers is very vast and is emerging in every field of application such as industry [103], biomedical [104], scientific [105] and high technology [106,107]. The polymers possess the unique status that many of the physical properties can be generated out of this by tailoring the structure with different functional radicals. The life giving DNA is the best example for this. There are insulating polymers like polytetrafluroethylene, common rubber, polystyrene, semiconducting polymers like cis,trans polyacetylene, poly-thiophene, polyvinyl carbazole and conducting polymers like doped polyacetylene, $(SN)_x$ and poly copper acetyl acetonate. The use of polymers is very common in day to day life and in high technology. The properties and uses are extensively described in recent reviews [108-110].

Eventhough switching is investigated well in inorganic glass systems, this study is sparse in polymer films. Since the polymers are numerous with varying molecular weight and properties, the investigation for stable switching in polymer films is justified. The communication (threshold aspect) and the storage (memory aspect) in living beings is a sort of switching in biological enzymatic polymers. The investigation in switching is necessary to follow up and

understand the biological mechanisms of intelligence. Eventhough Ovshinsky worked in this direction, all the 'Ovonic' systems used were of inorganic origin. The field of polymers in this context would open up a new horizon.

The first switching like report in a polymer film is due to Gregor et al. [111,112] and is followed by a others [113,114]. Both threshold and memory switching are observed in polymer films. There is a close similarity between chalco-genide glass switching and polymer switching. The amorphous nature is common to both kind of materials. But generally polymers are more insulating. Carchano et al. [115] Segui et al. [74] and Pender [68] observed memory switching in polystyrene films. The same behaviour is found in polybenzene and polyacetylene films. The switching is explained due to carbon channel formation by pyrolysis of the polymer.

The low voltage switching studied by Pender [68] and subsequently by Sakai et al. [116] are reported to be of electronic origin. Filamental type of switching is also reported by Lacaze et al. [43]. They observed electroforming, negative resistance, electron emission and switching phenomena in poly acetonitrile and poly tetrahydrofuran films.

Threshold switching is reported in many polymers. Baessler et al. [117] observed this in mylar films, Henisch et al. [47] observed in poly methyl methacrylate, polyethyl-methacrylate and polybutyl methacrylate and Hogarth [118] in poly propylene. Henisch et al. [47] conducted a series of investigations regarding dependence of electrodes, contact thrust on variation of $V_{th}$ and zero voltage resistance. They found that these depend on the dissipated power. As a general rule low power dissipation leads to more constant $V_{th}$ values. The switching is due to the injected charge carriers and space charge. The presence of space charge is found by the capacitance variation with the applied field.

Memory switching is reported in evaporated poly-acrylonitrile films [48], poly-N-vinyl carbazole [94] and organometallic polymer of copper acetyl acetonate. Switching in polyacrylonitrile and poly-N-venyl carbazole is explained due to the ionisation of traps present while in the case of poly copperacetyl acetonate [35] the mechanism is not clearly brought out. This film showed wide range of conductivities from $10^{-10}$ ohm$^{-1}$cm$^{-1}$ to $10^4$ ohm$^{-1}$cm$^{-1}$ depending on power rate in the preparation of the film. These films with conductivity $10^{-5}$ to $10^{-2}$ ohm$^{-1}$cm$^{-1}$ showed bistable switching. This switching

is similar to the Mott transition observed for $Sb_2S_3$ crystals when one per cent excess antimony is present and subjected to electric field.

In some cases light induced switching [119] is possible by keeping at a particular bias. Polythiophene is such a polymer. This can be utilized in opto electronic coupling applications. There are many other photoconductive polymers. Photo memory is also found in viologen vinyl pyrrolidone co-polymers [120].

The present work is mainly on switching investigations in plasma polymerised polymer thin films. Plasma being the raw material of the universe there is every hope of discovering new materials to emerge from plasma polymerisation technique. This method is becoming a fundamental technique for preparing a variety of functional organic thin films which are superior in many ways. They are generally chemically inert, thermally stable and mechanically tough. These polymers find a variety of potential applications like protective coatings [121] passivation layers [122], electronic applications [102], perm selective membranes [123] and many biomedical applications [124].

The importance of switching investigation arises both from an indepth understanding of the phenomenon as well as possible applications. The investigations are being pursued with vigour and new results emerge due to the present day interest in material research.

# REFERENCES

1. L.Bruning haus, Compt.Rend.Acad.Sci. **188** (1929) 1386.

2. J.G.Simmons and R.R.Verderber, **A301** (1967) 77.

3. S.R.Ovshinsky, Phys.Rev.Lett. 21 (1968) 1450.

4. A.D.Pearson, W.R.Northover, J.F.Dewald and W.F.Peek,Jr., Advances in Glass Technology, Plenum Press, New York, 1962.

5. B.T.Kolomiets and E.A.Lebedev, Radio Technik, 8 (1963) 2097.

6. N.F.Mott, **Festkorperprobleme**, 9 (1969) 22.

7. G.Dearnaley, A.M.Stoneham and D.V.Morgan, Rep.Prog.Phys. **33** (1970) 1129.

8. G.Jones and R.A.Collins, Thin Solid Films, **40** (1977) L15.

9. C.Feldman and K.Moorjani, J.Non-Cryst.Solids, 2 (1930) 82.

10. R.S.Potemper, T.O.Poehler and D.O.Cowan, Appl.Phys.Lett. **34** (1979) 405.

11. A.K.Bandyopadhyay, S.Chatterjee and S.V.Subramanyam, Nucl. Phys.Solid State Physics, C22 (1979) 251.

12. H.J.Hovel, Appl.Phys.Lett. **17** (1970) 141.

13. A.Moser, Appl.Phys.Lett. **20** (1972) 244.

14. H.Okushi, A.Matsuda, M.Saito, M.Kikuchi and R.Y.Hirai, Solid State Commun. **11** (1972) 283.

15. Lewin Crottoru and E.Gunbaum, Thin Solid Films, **67** (1980) L9.

16. Y.Hiroze and H.Hirose, Appl.Phys. **47** (1976) 2767.

17. J.C.Bernede, A.Conan, E.Fouesnant, B.E.Bouchairi and Goureaux, Thin Solid Films, **97** (1982) 165.

18. J.Bardeen and W.H.Brattain, Phys.Rev. **74** (1949) 230.

19. J.Tauc, Phys.Today, October 1976, 23.

20. L.O.Hill, Transistor Switching Circuits, Lloyd P.Hunter (Ed.), Handbook of Semiconductor Electronics, McGraw-Hill Book Co., New York, 1970.

21. S.M.Sze, Physics of Semiconductor Devices, Wiley Eastern Ltd., New Delhi, 1983.

22. T.W.Hickmott, J.Appl.Phys. **33** (1962) 2669.

G.S.Kreynima, L.N.Selivanou and T.J.Shumskala, Radio Engg.Elect.Phys. 5 (1960) 219.

R.A.Collins and R.D.Gould, Solid State Electron. 14 (1971) 801.

C.A.Hogarth and T.Iqbal, Phys.Stat.Solidi (a) 65 (1981) 11.

J.G.Gazso, Thin Solid Films, 21 (1974) 43.

C.A.Hogarth and M.Zor, Thin Solid Films, 27 (1975) L5.

R.R.Sutherland, J.Phys.D.Appl.Phys. 4 (1971) 468.

A.K.Ray and C.A.Hogarth, Int.J.Electronics, 57 (1984) 1.

N.F.Mott, Can.J.Phys. 34 (1956) 1356.

B.Gudden and W.Schottky, Z.Tech.Physik, 16 (1935) 325.

E.C.McIrvine, J.Phys.Chem.Solids, 15 (1960) 356.

L.Gildart, J.Non-Cryst.Solids, 15 (1970) 240.

R.K.Sadhir and W.James, Thin Solid Films, 97 (1982) 17.

Y.Osada, K.Yamada and I.Yoshizawa, Thin Solid Films, 14 (1969) 280.

36. S.R.Ovshinsky, U.S.Patent 3, 271, 591, Sept.6, 1966.

37. H.K.Henisch, Appl.Phys.Letters, **24** (1974) 589.

38. H.J.Hovel and J.J.Urgell, J.Appl.Phys. **42** (1971) 5076.

39. A.E.Owen, P.G.LeComber, W.E.Spear and Hajito, J.Non-Cryst. Solids, **59&60** (1983) 1273.

40. J.I.Dewald, A.D.Pearson, W.R.Northover and W.F.J.Peck, Electrochem.Soc. **109** (1962) 243C.

41. D.L.Eaton, J.Am.Ceram.Soc. **47** (1964) 554.

42. T.W.Hickmott, J.Appl.Phys. **36** (1965) 1885.

43. P.C.Lacaze, J.E.Durois and G.Tourillon, Thin Solid Films, **66** (1980) 159.

44. W.O.Buckly and Holmberg, Private communication, 1972.

45. P.J.Walsh, J.E.Hall, Nicolaides, R.Defeos, P.Calella, J.Kuchmas and W.Doremus, J.Non-Cryst.Solids, **2** (1970) 107.

46. R.Harberland, R.Karnan and F.Repp. Frequenz (1970) 212.

47. H.K.Henisch and J.A.Mayers, Thin Solid Films, **51** (1978) 265.

48. J.A.Mayers, J.Non-Cryst.Solids, **79** (1986) 57.

49. Hemamalini Naik and S.V.Subramanyam, Pramana, **26** (1986) 61.

50. R.L.Remke, R.M.Walser and R.W.Bena, Thin Solid Films, 97 (1982) 129.

51. H.K.Henisch, R.W.Pryor and Vendura,Jr., J.Non-Cryst.Solids, 8-10 (1972) 415.

52. S.H.Lee H.K.Henisch and W.D.Burgess, J.Non-Cryst.Solids, 8-10 (1982) 422.

53. K.R.Shanks, J.Non-Cryst.Solids, 2 (1970) 504.

54. H.K.Henisch and R.W.Pryor, Solid State Electron 14 14 (1971) 705.

55. D.R.Haberland, Solid State Electronics, 13 (1970) 207.

56. R.W.Pryor and H.K. Henisch, J.Non-Cryst.Solids, 7 (1982) 181.

57. H.Fritzsche, Amorphous and Liquid Semiconductors, J.Tauc (ed.), Plenum Press, New York, 1974, 313.

58. V.Foek, Arch.Electrotech. 19 (1927) 71.

59. K.W.Boer, E.Jahnke and E.Nebauer, Phys.State Sol. 1 (1961) 231.

60. J.Kaplan and D.Alder, Appl.Phy.Lett. 19 (1971) 418.

61. R.W.Keyes, Comments on Solid State Phys. 4 (1971) 1.

62. D.M.Kroll and M.H.Cohen, J.Non-Cryst.Solids, 8-10 (1972) 254.

63. A.D. Pearson and C.E. Miller, Appl.Phys.Lett. **14** (1969) 280.

64. H.J.Stocker, Appl.Phys.Lett. **15** (1969) 55.

65. T.W.Hickmott, J.Vac.Sci.Technol. **6** (1969) 828.

66. Herbert F.Matare, Defect Electronics in Semiconductors, Wiley Interscience, New York, 1971.

67. R.Vogel, Appl.Phys.Lett. **14** (1969) 216.

68. L.F.Pender and R.J.Fleming, J.Appl.Phys. **46** (1976) 3426.

69. J.C.Bernede, A.Conan, E.Fouesnant, B.E.L.Bouchairi and G.Gloureaux, Thin Solid Films, **97** (1982) 165.

70. Y.Hirose and H.Hirose, J.Appl.Phys. **47** (1976) 2767.

71. J.Swaitek, Thin Solid Films, **41** (1977) 5.

72. D.V.Dearnaley W.Morgan and A.M.Stoneham, J.Non-Cryst. Solids, **4** (1970) 593.

73. J.M.Wood Cock, J.E.Rulph, J.Non-Cryst.Solids,7 (1972) 236.

74. Y.Segui, Bui Ai and H.Carchano, J.Appl.Phys. **47** (1976) 140.

75. G.C.Vezzoli, Patric Calella and William Doremus, J.Appl. Phys. **44** (1973) 341.

76. N.F.Mott, Con.Temp.Phys. 10 (1909) 125.

77. N.F.Mott, Phil.Mag. 24 (1971) 911.

78. D.Alder, Private communication, 1972.

79. S.H.Lee, Appl.Phys.Lett. 21 (1972) 544.

80. N.K.Hindley, J.Non-Cryst.Solids, 5 (1970a) 17.

81. K.W.Boer G.Dohler and S.R.Ovshinsky, J.Non-Cryst. 4 (1970) 573.

82. H.Fritzsche and S.R.Ovshinsky, J.Non-Cryst.Sol. 2 (1970a) 393.

83. H.K.Henisch, E.A.Fagen and S.R.Ovshinsky, J.Non-Cryst. 4 (1970) 673.

84. M.A.Lampert, Phys.Rev. 125 (1962) 126.

85. W.Van Roos Broeck, Phys.Rev.Lett. 28 (1972) 1120.

86. C.S.Athwal, R.V.Latham, J.Phys.D.Appl.Phys. 17 (1984) 1029.

87. A.Weinreb, N.Ohana and A.A.Braner, J.Chem.Phys. 43 (1965) 701.

88. H.J.Stocker, C.A.Barlow Jr. and D.F.Weirauch, J.Non-Cryst. 4 (1970) 523.

89. B.T.Kolomiets, A.A.Lebedev, N.A.Rogachev and V.S.Punt, Sov.Phys.Semicond. 6 (1972) 167.

90. G.C.Vezzoli, P.J.Walsh, P.J.Kisatsky, L.W.Doremus, J.Appl. Phys. **45** (1974) 4534.

91. H.K.Henisch and W.R.Smith, Appl.Phys.Lett. **24** (1974) 589.

92. Marvin M.Cohen, Morris Campi and James D.Penar, J.Non-Cryst.Solids, **2** (1970) 91.

93. M.Datta, P.N.Banerjee and D.L.Bhattacharya, J.Instn. Electron. & Telecom.Engrs. **26** (1980) 122.

94. J.Swaitek, Thin Solid Films, **61** (1979) 321.

95. Y.Sadaoka and Y.Sakai, J.Chem.Soc.Faraday Trans.II, **72** (1976) 1911.

96. N.G.Patel, J.Mater.Sci. **22** (1986) 2097.

97. Z.T.Al. Ahhan and C.A.Hogarth, J.Mat.Sci. **22** (1987) 3698.

98. R.H.Bube, G.A.Dussel, C.T.Ho and L.D.Miller, J.Appl. Phys. **37** (1966) 21.

99. C.Chiang, Solid State Commun. **39** (1981) 111.

100. R.P.Hall, M.F.Hundley and A.Zettel, Physica **143B** (1986) 152.

101. K.Yoshino, K.Tanimura, Y.Yamamoto, K.Kaneto and Y.Inuishi, Technol.Repts., Osaka University, **28** (1978) 1430.

102. Hisashi Ueda, J.Polymer Sci. Pt.A, **27** (1989) 263.

103. Jacqueline I.Kroschwitz, Polymers: An Encyclopediac Source Book of Engineering: Properties, Wiley, New York, 1987.

104. Charles G.Gebelain, Advances in Biomedical Polymers, Plenum Press, New York, 1987.

105. Jerold Shultz, Polymer Material Science, Prentice Hall Inc., New Jersey, 1974.

106. A.Knop and W.Seheib, Polymers Properties and Applications, Springer Verlag, Berlin, 1979.

107. Murrae J.Bowden and S.richard Turner, Polymers for High Technology Electronics and Photonics, Washington, Am.Chem. Soc., 1987.

108. Stephen T.Kowel, Richard Selfridge, Charles Eldering, Normal Matloff, Pieter Stroeve, Brian G.Higgins, M.P.Srinivasan and Lawrence B.Coleman, Future Applications of Ordered Polymeric Thin Films, Thin Solid Films, 152 (1987) 377.

109. Terene W.Barrett, Physical Properties of Ordered Ultra Thin Films, 1987.

110. P.Le Barney, Thin Solid Films, 152 (1987) 99.

111. L.V.Gregor, Thin Solid Films, 2 (1968) 235.

112. L.V.Gregor and L.H.Kaplan, Thin Solid Films, 2 (1968) 95.

113. J.Kevorkian, M.M.Labes, D.C.Larson and D.C.Wu, Trans. Faraday Soc. **51** (1971) 139.

114. W.P.Ballard and R.W.Christy, J.Non-Cryst.Solids, **17** (1975) 81.

115. H.Carchano, R.Lacoste, Y.Segui, Appl.Phys.Lett. **19** (1971) 414.

116. Y.Sakai, Y.Sadaoka,and C.O.Okada,J.Mater.Sci. **19** (1984) 1333.

117. H.Baessler, N.Richi, W.Spannring, Z.Angew.Phys. **27** (1969) 321.

118. C.A.Hogarth, T.Iqbal, Int.J.Electron. **53(2)** (1982) 129.

119. K.Yoshino, R.Sugimoto, J.G.Rabe and W.F.Schmidt, Jpn.J. Appl.Phys. **24(1)** (1985) L33.

120. H.K.Kamogawa and Amamiya, J.Polym.Sci.Polym.Chem. **23** (1985) 2413.

121. K.Harada, J.Appl.Polym.Sci. **26** (1981) 3707.

122. R.Zahn, J.Acoust.Soc.Am. **69** (1981) 1200.

123. H.Yasuda and C.E.Lamaze, J.Appl.Polym.Sci. **20** (1976) 543.

124. A.Mizumoto and Y.Osada, J.Appl.Phys. **59** (1986) 1776.

# Chapter 2

## INTRODUCTION TO POLYMERS, PLASMA POLYMERISATION

## AND RELATED EXPERIMENTAL SET UP

## Abstract

A general description to polymers and plasma polymerisation is given. Methods of preparation of thin films by plasma polymerisation are briefly described. The electrical and electronic behaviour of polymer films are discussed. A description of a sweep voltage generator, used for the switching investigations, is given. The design and fabrication details of a metal vacuum chamber used for electrical study are also presented. The description of the electrode coating set up and the evaporation procedures are discussed. The experimental set up used for the switching investigation is also described.

## 2.00 INTRODUCTION

Polymers are long chain molecules linked together by covalent bonds to form macromolecules [1]. The small unit that repeats in the covalent bonding is known as the monomer. Certain polymers are linearly bonded and are known as linear polymers like polyacetylene and polyethylene. There are branched net work polymers as well as cross linked polymers formed due to side reactions. In these polymers, more reactive groups will be present. Polymers are generally disordered materials and are considered amorphous due to the lack of definite crystal structure and molecular weight. Large variations in molecular weight are observed depending on the conditions of polymerisation [2]. The interaction between the polymer molecules is very weak eventhough strong bonds are present in the main chain. The polymers possess the unique status that their properties can be changed by tailoring different functional group to the main chain. This can be effected by co-polymerisation [3,4], or by adding functional impurities at the time of polymerisation.

Polymers of organic, inorganic [5,6] and organo-metallic [7] origin can be prepared under suitable conditions. These materials are generally insulators but many semiconducting [8,9] and conducting [10] polymers are also reported. The properties are widely varied depending on the degree of polymerisation structure, functional radicals present and dopants, if present.

2.10   DESCRIPTION OF POLYMERISATION, ELECTRICAL AND

ELECTRONIC BEHAVIOUR OF POLYMERS

2.11   Polymerisation

The polymerisation of monomer can be effected by

chemical and physical methods. There are two types of poly-

merisation--one is condensation polymerisation or step reaction

and the other is addition polymerisation or chain reaction.

In the first case, two polyfunctional molecules condense to

form a larger molecule with the elimination of a small molecule,

like water. In the addition polymerisation, the free radicals

of monomers are joined by a chain reaction [1]. A radical is

formed when there is an unpaired electron present in  the

monomer unit. The radical initiated process is prominent in

the physical method of polymerisation.


The free radical polymerisation proceeds in three

steps--the initiation, propagation and termination. Two

monomer radicals react to give a dimer radical. This dimer

radical again react with a monomer radical and the process

is continued until a disproportionation or recombination

occurs for a termination of the chain reaction. Higher the

initiator concentration of free radicals, faster is the

reaction and also the termination. The free radicals  are

formed by electric field or ionising radiations such as gama rays, UV radiation or energetic electron beams.

## 2.12 Plasma polymerisation

Plasma polymerisation [11] is based on free radical polymerisation method. This method is highly efficient, economic and is superior to many other methods. The films prepared thus are pin hole free, chemically stable and insoluble in many solvents. Many of the organic, inorganic and organometallic materials are easily polymerised by this method. In plasma polymerisation, free radicals may be formed by the cleavage of single bonds, double bonds or tripple bonds and ring opening by ionising agents. The important methods of plasma polymerisation are the following. Silent discharge, microwave discharge, radio frequency discharge, low frequency discharge and direct current discharge. Bradley and Hammes [12] have polymerised a large number of monomers by this method and studied their electrical properties. A review of plasma polymerisation is given by Millard [13].

Silent discharge polymerisation utilizes a co-axial configuration of discharge tubes usually made of glass or quartz. The alternating (50 Hz) high voltage (5 to 10 KV) is fed between the co-axial tubes preventing the discharge electrodes from making a direct contact with the vapour. The discharge takes place at a vacuum of $\bigcap$ 0.6 torr.

Microwaves can be utilised to generate plasma discharge at comparatively high pressure of $\cap$ 1 torr. The microwaves from a Klystron or magnetron are fed into the resonant cavity enclosing the reactor. This technique is more successful for inorganic compounds.

Plasma polymerisation can be carried out very easily by using radio frequency in the range 1-200 MHz. This method does not require internal electrodes as the radio frequency is capabable of propagation through glass or quartz tube. The RF power is fed externally by capacitive or inductive coupling. The pressure is of the order of 0.6 torr.

A very simple method of plasma polymerisation is the low frequency (50 Hz) high voltage (500-1500 V) glow discharge. The electrodes are directly in contact with the vapour. The discharge takes place for a pressure range 0.1 to 1 torr. Instead of an alternating current, direct current discharge can also be used to generate plasma. In this case the polymer deposition mainly takes place on the cathode.

2.13  Electronic behaviour of polymers

Based on the electronic behaviour, polymers are divided into two classes. One with saturated or unsaturated back bones but without pendant group. In this the electronic

properties [14-16] are heavily controlled by the main chain with covalent bonds. Examples are polyacetylene and poly-ethylene. The other class consists of saturated or unsaturated backbone but with attached aromatic chromophores like in polystyrene and polyvinyl carbazole. In this class, the electronic behaviour is mainly due to the attached chromo-phores and is like isolated aromatic molecules. The inter-action between the pendant groups and the main chain results in much lower ionisation potential than saturated backbone structures. This is a major factor that controls the electrical properties of this class of polymers.

The excited states in a polymer consists of localised states, Frenkel excitons, Wannier excitons, and charge carriers (holes and electrons). Polymers are generally amorphous and consist of several structural defects and impurity centres. The localised excited states are generally frozen type and remain in the same site, if the interaction with them is small. The Frenkel excitons are bound electron hole pair and is neutral and mobile. The Wannier excitons consists of electron hole pair involving different molecules. Unlike Frenkel excitons, these are also mobile. In polymers, the major energy transfer is taking place through these excitons rather than through free holes and electrons. The major conduction process becomes hopping in polymers.

The ionic excitation states are described by many authors. The ionisation of the highest occupied level and binding energy of the lowest unoccupied level for different polymers are given elsewhere [17]. The energy levels are first observed directly by carrier photo emission from the metal electrodes in polyvinyl carbazole.

Different workers have analysed the energy levels of polymers by the conductivity measurements [18]. Techniques like, infra red, ultra violet and visible spectroscopy and thermally stimulated depolarisation currents are very commonly used to study the energy levels of a polymer. The doping of the polymers can be used to introduce new energy levels.

2.14 Electrical properties of polymers

The general conduction mechanisms found in insulators are also applicable to polymers. These are (a) direct tunnelling from one electrode to the other (b) injection of carriers into the conduction or valence band by thermionic or schottky emission (c) tunnelling of carriers through the barrier (field emission) (d) Poole-Frenkel emission mechanism in the bulk; (e) scattering of carriers in the conduction band and (f) hopping of carriers from trap to trap. These are reviewed by many authors [19-21]. Ionic conduction mechanism [22] are also found in polymers. The conductivity in polymers are found to vary from metallic [23, 4] to very high insulating [24].

Of the major electronic conduction mechanisms, Poole-Frenkel [25] effect, Schottky [26] emission, hopping [27] and space charge formation are very much prominent in plasma polymers. Poole-Frenkel effect is a bulk phenomenon while Schottky emission is an electrode limited process. Both are field assisted processes resulting in the lowering of potential barriers. The general expression for current density can be written as

$$J = AT^2 \exp \frac{(\beta V^{\frac{1}{2}} - \emptyset)}{KT} \qquad (2.01)$$

where A is the Richardson constant, K is the Boltzmann constant, T the absolute temperature and $\emptyset$ the potential barrier. The coefficient $\beta$ is different for both Schottky and Poole-Frenkel conduction. The Schottky coefficient $\beta$ is given by the relation

$$\beta = \frac{e^3}{4\pi \, \epsilon \, \epsilon_0} \qquad (2.02)$$

and in the case of Poole-Frenkel effect it is given by

$$\beta = \frac{e^3}{\pi \, \epsilon \, \epsilon_0} \qquad (2.03)$$

Here e is the electronic charge, $\epsilon$ is the high frequency dielectric constant and $\epsilon_0$ the permittivity of free space.

The plot log I versus log V gives the same slope$\left(\sim \frac{1}{2}\right)$ for Schottky and Poole-Frenkel conduction. To differentiate, a comparison of the theoretical and experimental results are often adopted. Since Schottky emission is an electrode limited process, by using different electrodes differing in work functions this process can be distinguished from the Poole-Frenkel effect.

At lower fields, ohmic conduction is expected. The current density for ohmic region, A-B as in Fig.2.01 is $J_{ohm} = n_o e \mu \frac{V}{d}$ where $n_o$ is the initial concentration of charge carriers, $\mu$ and v are the mobility and voltage. But at higher fields, space charge limited conduction ((SCLC) is common in polymer films [28,29]. Lampert [30] and Rose [31] have shown that space charge limited currents give information about the traps present. In the space charge region tunnelling or injection is not the rate limiting process. When the injected charge carriers are more than the thermally generated carriers, space charge limited currents are observed. The excess charge accumulates near the electrodes or in the bulk material impeding the flow of charges. The two conditions for space charge limited currents are (1) at least one electrode must have ohmic contact to the insulator and (2) the insulator must be one with relatively less traps. The expression for SCLC conduction for shallow traps, (B-C) is given by:
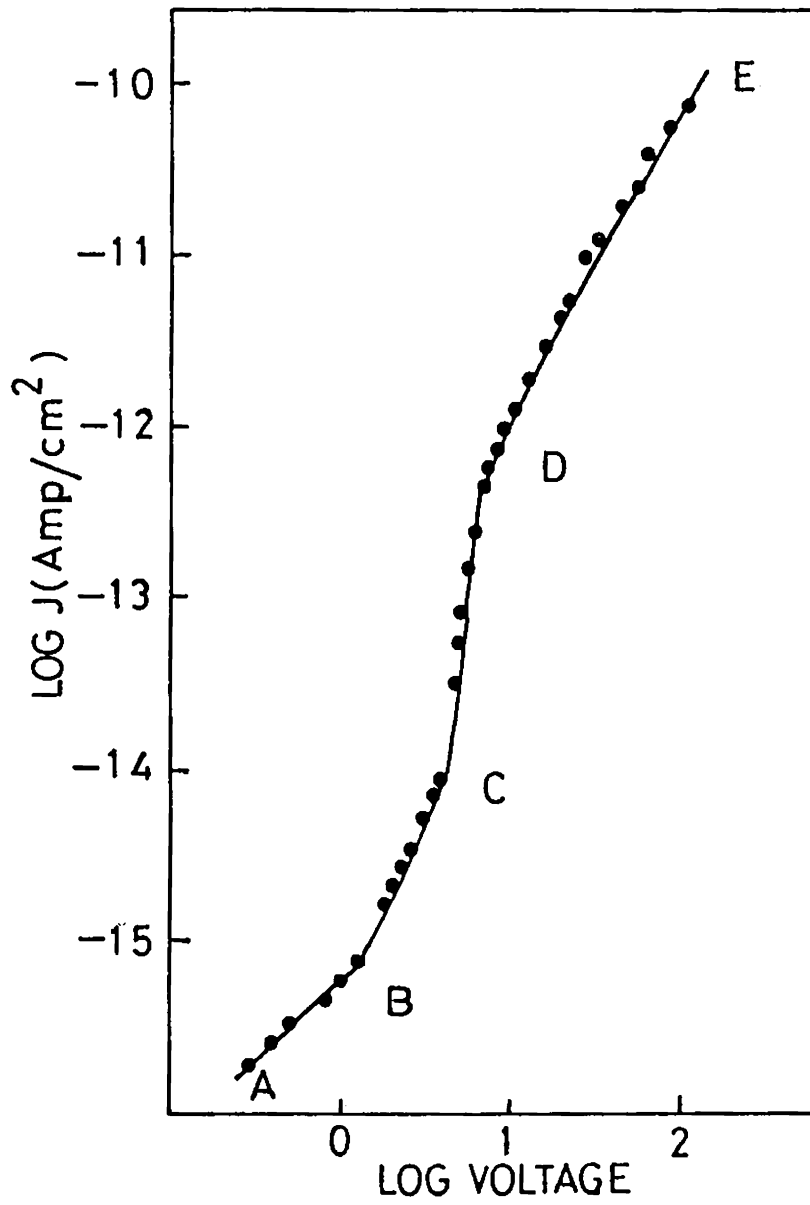
Fig.2.01. Typical log I versus log V plot illustrating different conduction regions.

$$J_{SCLC} = \frac{9}{8} \frac{\varepsilon \mu v^2}{d^3} \qquad (2.04)$$

Here $\varepsilon$ is the dielectric constant and d the thickness of the specimen. Due to the presence of traps, the injected carriers are trapped to some extent and is represented by $\theta$ which is given by

$$\theta = \frac{N_c}{N_t} \exp \frac{-E_t}{KT} \qquad (2.05)$$

where $N_c$ is the effective density of state in the conduction band, $N_t$ and $E_t$ the trap density and trap level energy below the bottom of the conduction band. For shallow and trap free SCLC region $\theta$ is unity [32]. The change over of ohmic region to shallow trap region occurs at an voltage

$$V = \frac{8}{9} \frac{n_o e d^2}{\varepsilon} \qquad (2.06)$$

As the field is further increased, the Fermi level moves upward close to the conduction band and the existing traps become deep and are not effective. The injection of charges fills the traps and a trap filled region C-D is observed. The trap filled limit voltage is given [33] by

$$V_{TFL} = \frac{e \, N_t \, d^2}{2 \, \varepsilon} \qquad (2.07)$$

Any further increase of voltage will sharply increase the current and the current density is expressed as $J \propto V^n$. This increase in current would lead to a threshold or memory switching action or a dielectric break down. These aspects are discussed in the subsequent chapters.

## 2.20 FABRICATIONS

### 2.21 Fabrication of a sweep voltage generator

A slowly and steadily increasing voltage source is essential for the investigation of switching studies. A sweep voltage generator is such a source, producing linear variation of output voltage with time. The basic idea of a sweep generator is letting a capacitor charge or discharge through a resistor. In the case of repetitive sweeps, when the instantaneous voltage reaches a particular value the capacitor is made to switch abruptly through a voltage controlled switch.

The sweep voltage source is realized by the integrating operation of an IC-741. This is a general purpose high gain operational amplifier designed for a wide range of analog applications [34]. It has many advantages like output short circuit protection, internal phase compensation, latch free operation, wide range common mode and differential mode signal ranges and low off set voltage nulling capacity. It consists of a differential input amplifier that effectively drives a

gain and a level shifting stage having a complementary emitter follower circuit. The operational amplifier is employed in a Miller Integrator circuit which generates a precise and linear sweep voltage. The output is proportional to the integral of the input voltage that is the product of amplitude and duration of the input. The schematic diagram is as in Fig.2.02. The time varying current that flows through resistor R is given by

$$i = \frac{V_i}{R} \tag{2.08}$$

This current will flow through the feed back capacitor and an voltage appears across its terminal. Since one end of the capacitor is at the virtual ground point, the output voltage of the amplifier equals the capacitor charging voltage. Then the output voltage $V_o$ is given by

$$V_o = \frac{-1}{C} \int i\, dt$$

$$= \frac{-1}{RC} \int v\, dt \tag{2.09}$$

Thus $V_o$ is proportional to the integral of the input voltage. For a constant input voltage $V_i$, $V_o$ is given by

$$V_o = \frac{-V_i}{RC} \int dt$$

$$= \frac{-V_i}{RC} t \tag{2.10}$$

Thus the output voltage rises linearly with time or

$$t = \frac{-V_o \, RC}{V_i}$$  (2.11)

Hence for a constant C, the sweep time can be changed either by change of input voltage or resistance. The sweep time is adjusted by a 1 M$\Omega$ potentiometer and the magnitude of output voltage is varied by a 100 K$\Omega$ potentiometer as shown in Fig.2.03. The constant power supply of +12 and -12V is fabricated using a 18-0-18 (1 amp) step down transformer, bridge rectifiers, capacitors, zener diodes and resistors. Both the power supply and sweep units were assembled on a single printed circuit board. The sweep time is in the range of 10 sec to 60 minutes. The minimum rate of change of voltage is 0.2 V/minute.

## 2.22 Metal vacuum chamber

The electrical switching investigations are carried out using a metal vacuum chamber as shown in Fig.2.04. This chamber helps to prevent external electrical disturbances, effects of light and ambient atmospheric effects. This chamber consists of a metallic outer tube of 16 cm diameter and a height of 30 cm. The top and bottom of the chamber are vacuum sealed by circular flanges. This is effected by the use of neoprene O-rings. There are ports for pumping and connecting
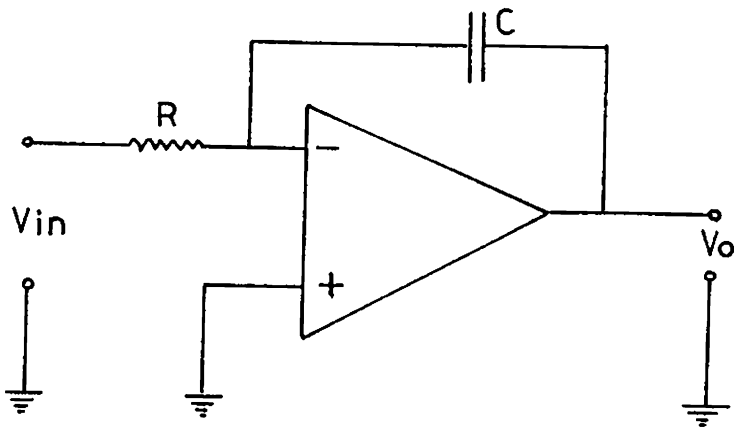
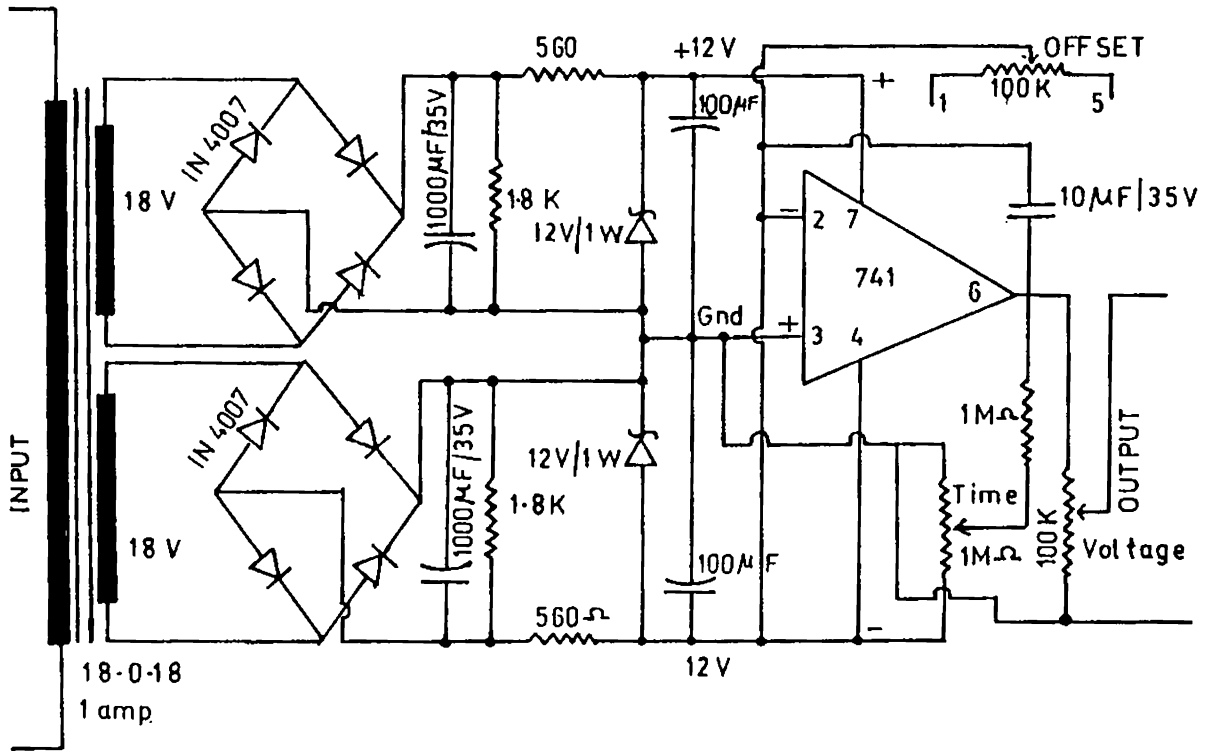Fig.2.02. Schematic diagram of operational integrator.



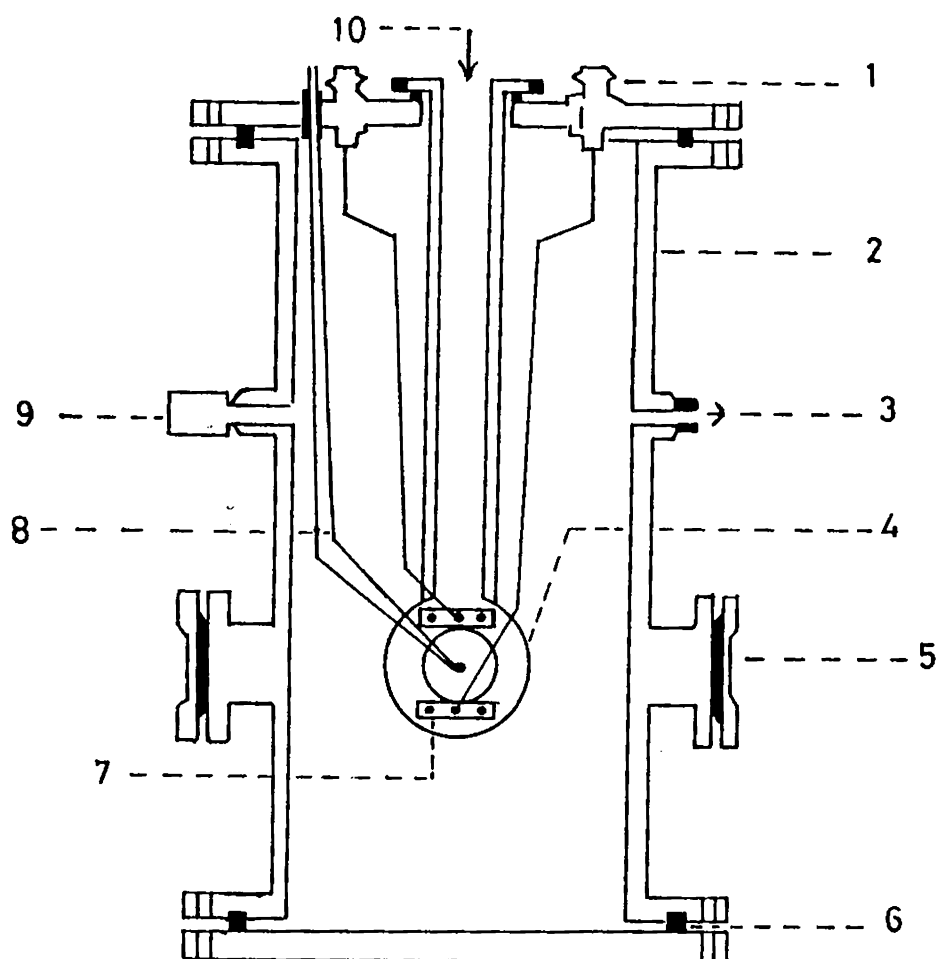Fig.2.03. Circuit diagram of sweep voltage source.

Fig.2.04. Schematic diagram of metal vacuum chamber used
for electrical measurements. 1 - electrical
feed through, 2 - metal chamber, 3 - to guage,
4 - sample holder with heater, 5 - glass window,
6 - neoprene O-ring, 7 - teflon insulation,
8 - thermocouple, 9 - air inlet valve,
10 - liquid $N_2$ port.

guages on the sides of the chamber. The top flange holds the specimen connecting part and is vacuum sealed. The specimen holder consists of a liquid nitrogen trap made of a steel tube of length 12 cm. At the bottom end a circular section holds the specimen. The liquid nitrogen cavity also is extended to the circular section. The electrical connections are made to the electrodes of the specimen by spring loaded copper blocks with teflon sheets. The teflon sheets are spring loaded to keep tightly the copper blocks to the electrodes. The temperature of the specimen can be varied from -193 to 300°C by using liquid nitrogen and a 60 W electric heater. An iron constantan thermocouple is used to read the temperature of the specimen.

Two teflon feed throughs are used for the electrical connections and two other teflon feed throughs for the thermo-couple connections. The electrical connections are made through two shielded cable connectors and is connected to the copper blocks with teflon shielding. The whole chamber is properly earthed to avoid external pick up of noise. By using a rotary pump the chamber is evacuated to $10^{-2}$ torr. The pressure is read by a pirani guage. The temperature of the specimen is read by using a micro voltmeter connected to the thermo-couple leads. The electrical connections are made to the current reading and voltage reading systems attached to either an X-Y chart recorder or an oscilloscope.

## 2.23 Electrode preparation

The preparation of metal electrodes are made using evaporation under high vacuum ($10^{-6}$ torr). For the evaporation of aluminium, tungsten filaments are made use of, while a molebdenum boat is used for the evaporation of silver powder. This electrode coating unit consists of a backing rotary pump, a diffusion pump, baffle valves, liquid nitrogen trap and base plate holding high current feed throughs, pumping port and guage ports. An L-gasket tightly keeps the glass dome pressure tight to achieve the desired vacuum. The design details of the vacuum evaporation unit is given elsewhere [19] and is shown schematically in Fig.2.05.

The substrate is usually of glass which is cleaned thoroughly [35] and dried. This is kept horizontally above the filament or boat sources after proper masking. The masking can be made by using mica or steel strips. Due to the high current (100 amp and 10 V) the filament or boat is raised to high temperatures. This allows the evaporation of aluminium or silver under a vacuum of $10^{-5}$ torr. Many of the metals can be evaporated using this method.

A substrate with a suitable electrode is kept in the polymerisation set up. A desired polymer film is obtained on the electrode area after proper masking. Again this polymer
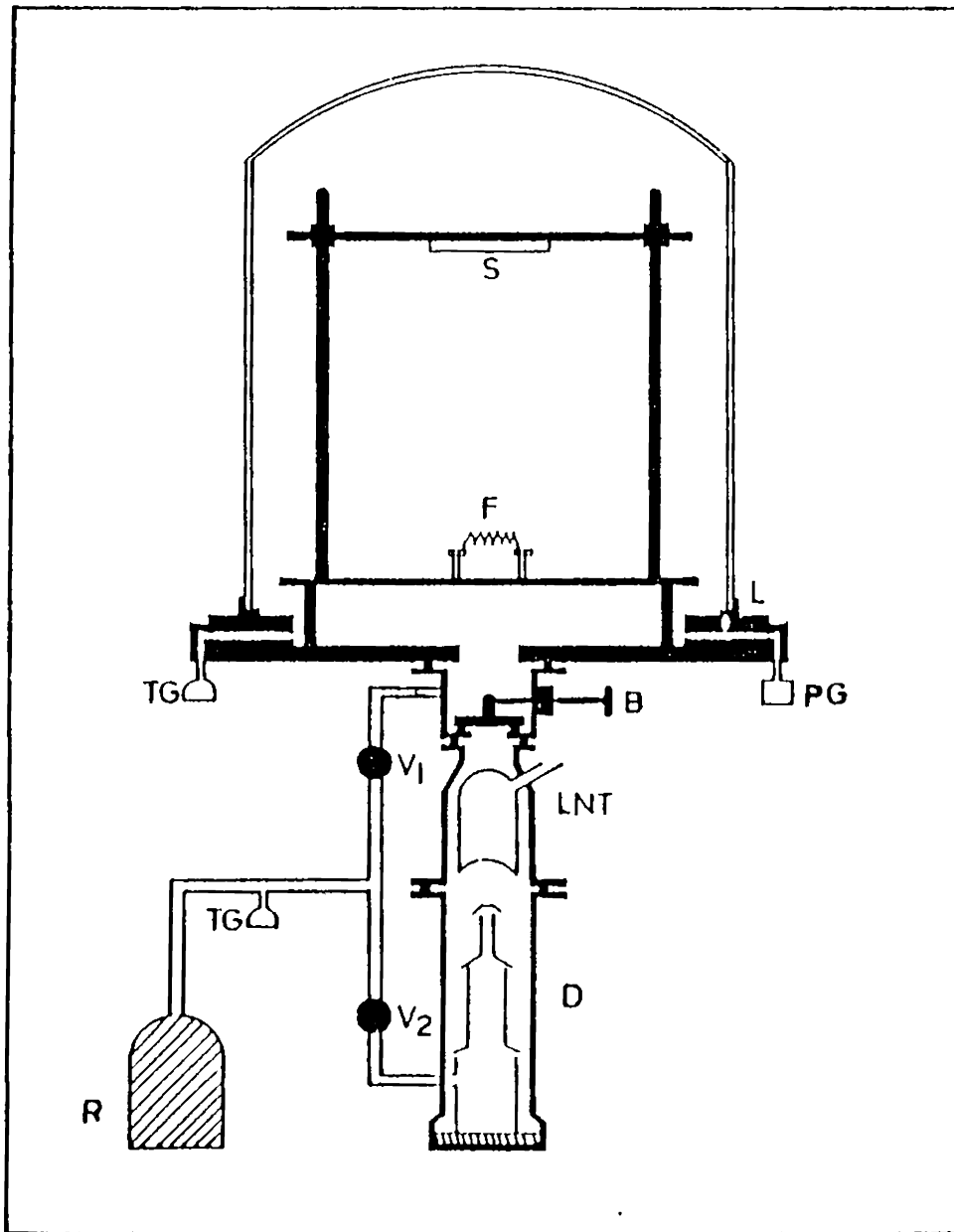
Fig.2.05. Schematic diagram of vacuum coating unit for the
evaporation of metal electrodes. D - diffusion
pump, LNT - liquid nitrogen trap, B - baffle valve,
PG - penning guage, L - neoprene L gasket,
S - substrate, F - filament, TG - thermocouple gauge,
R - rotary pump, $V_1$ - diaphragm valve for roughing
and $V_2$ - diaphragm valve for backing.

film is electrically sandwiched by evaporation of a counter electrode to form a metal-polymer-metal sandwich structure of one square centimeter area as in Fig.2.06. The prepared sandwich film on the substrate is kept in a vacuum desiccator to avoid deterioration of the film.

## 2.30 THICKNESS MEASUREMENT

### 2.31 The thickness measurement of electrodes

The thickness of the electrode material like silver or aluminium is found from the mass of the metal evaporated. If the source is considered as a point and evaporation takes place uniformly in all directions, then the mass received at a far away substrate will be $4\pi R^2 \rho t$ around a spherical surface. Hence the thickness t is given by the relation

$$t = \frac{m}{4\pi \rho R^2} \qquad (2.12)$$

Here $\rho$ is the density of the metal and R, the distance between source and substrate. For aluminium $\rho = 2.7$ gm/cc. Actually the tungsten helix is not a perfect point source and is only an approximation. In the case of a boat source the thickness $t = m/\pi \rho R^2$ is used.
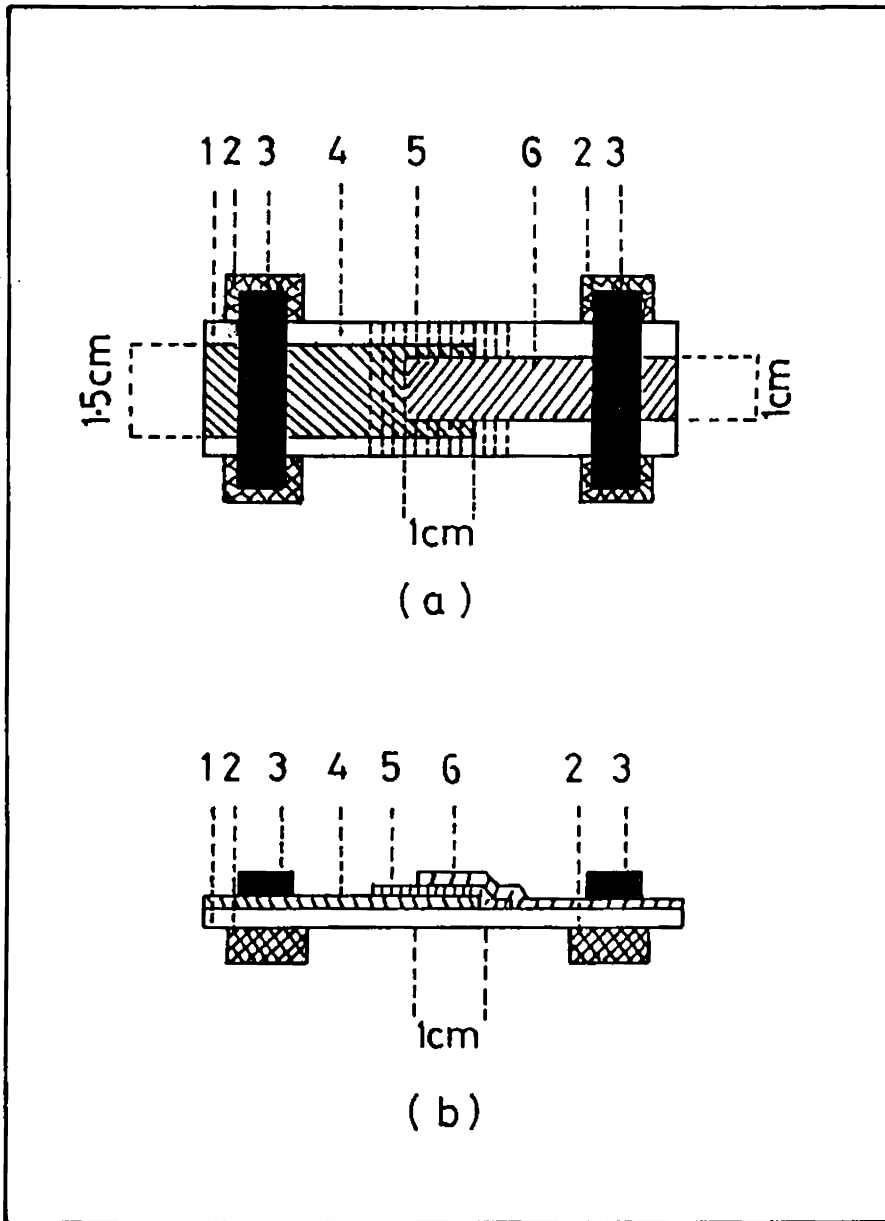
Fig.2.06. Schematic diagram of metal-polymer-metal structure.
(d) The top view and (b) the side view of the specimen. 1 - glass substrate, 2 - heating copper block, 3 - copper block for electrical connection, 4 - inner bound electrode, 5 - polymer thin film, and 6 - outer free electrode.

## 2.32 The thickness measurement of polymer film

The thickness of the polymer film is more accurately measured using optical interference method. The interference fringes are obtained when the monochromatic light beam is made to fall on partially reflecting surface which forms an air wedge with a fully reflecting surface. The Fizeau fringes are formed at spacing of $\lambda/2$ along the air wedge. If now a thin film step is there beneath the fully reflecting surface the fringes at the step will be shifted as a function of thickness of the step. The fringes must be perpendicular to the step. The shift will be fraction or more than the fringe spacing $\lambda/2$. Hence the shift $\triangle_N$ is equal to total shift/ fringe spacing. Hence the thickness of the step is given by

$$t = \frac{Shift}{Fringe\ spacing} \times \frac{\lambda}{2} \qquad (2.13)$$

Wiener [36] was the first who used this method and is now an absolute standard method for thickness measurement of thin films.

The experimental arrangement for the thickness measurement is as shown in Fig.2.07. The glass substrate with the thin film step and reflecting surface coating is as in Fig.2.08. A partially reflecting glass surface is placed on the substrate to form an air wedge. A green filter ($5461\overset{o}{A}$) with a mercury lamp offers the monochromatic light source S.
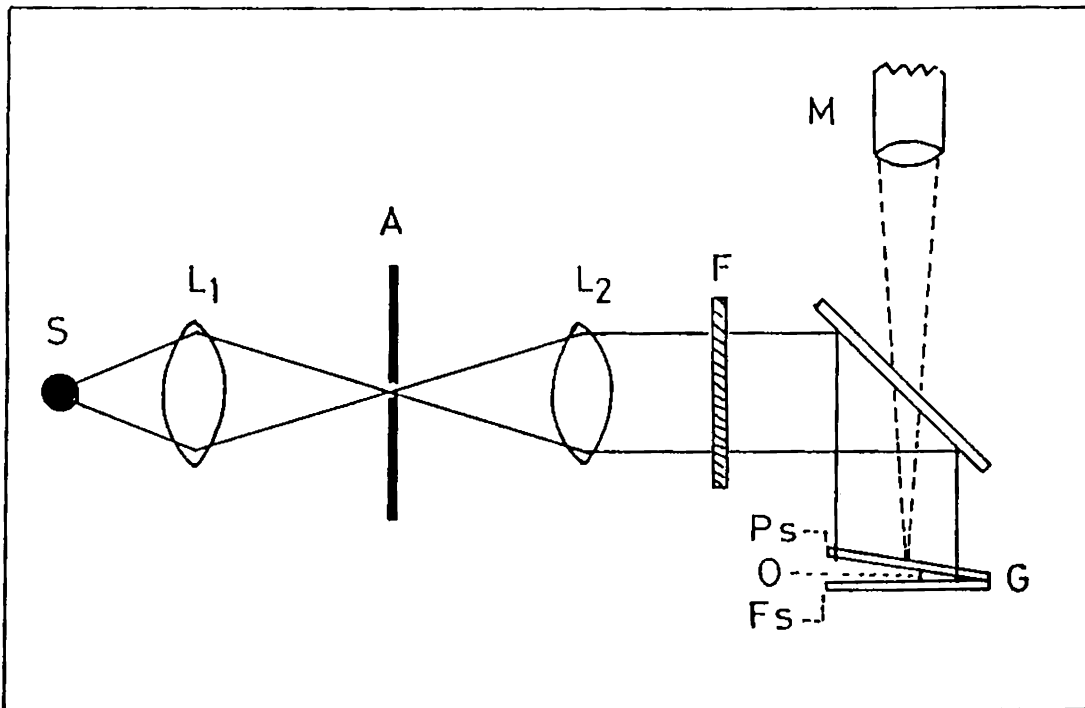
Fig.2.07   Experimental set up for the thickness measurement·
S - mercury source, L - lens system, F - Filter(5461Å)
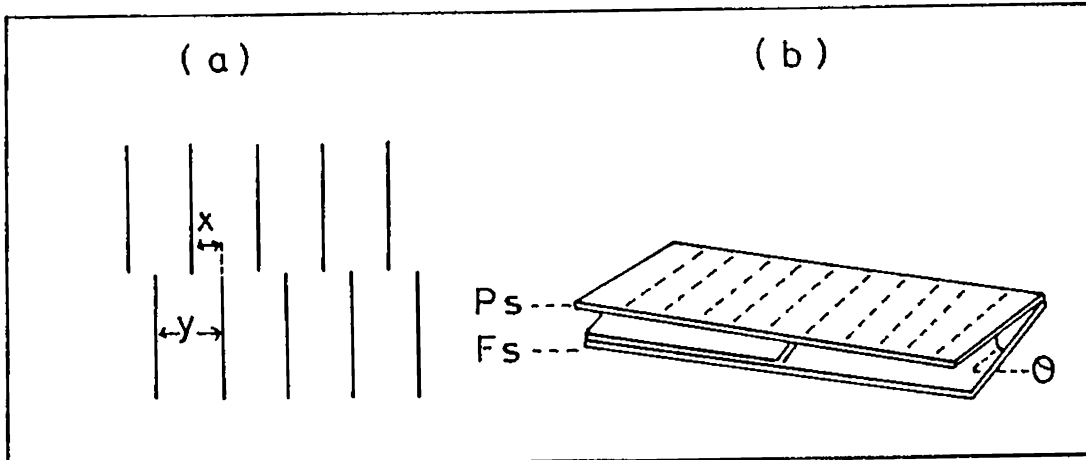A - apperture, G - glass substrate and M - travelling
microscope.



Fig.2.08   (a) The illustration of fringe shift, x- the fringe
shift, y - the fringe separation, (b) The air wedge,
Ps - partial reflecting surface, Fs - fully reflecting
surface,     - the wedge angle.

Using a circular apperture A and a system of lenses $L_1$ and $L_2$, the beam is made to fall parallel on the air wedge G. The fringes formed are clearly visible through a travelling microscope. It should be noted that the film with step and the partially reflecting surface are to be coated with the same material to avoid phase change and to obtain the same reflection from the two surfaces.

## 2.40 THE EXPERIMENTAL SET UP USED FOR SWITCHING INVESTIGATIONS

The experimental set up for switching studies consists of a steadily increasing linear sweep voltage source, a pulse generator and an X-Y chart recorder or a storage oscilloscope. The schematic diagram is shown in Fig.2.09. The sweep voltage is set for a linear rate of 0.5 V/minute. The voltage is fed to the specimen through a series resistor (0.1 to 1 $K\Omega$). This series resistor provides short circuit protection of the specimen. The voltage drop across the specimen is read by using a digital multimeter or a chart recorder. A small resistance of 1 to 100 ohms is used in series after the specimen. The potential drop across this resistor measures the rise in the current. This can be done after measuring the direct current by a multimeter and subsequently standardising the current axis in the X-Y chart recorder. Thus both current and the voltage across the specimen could be measured. The
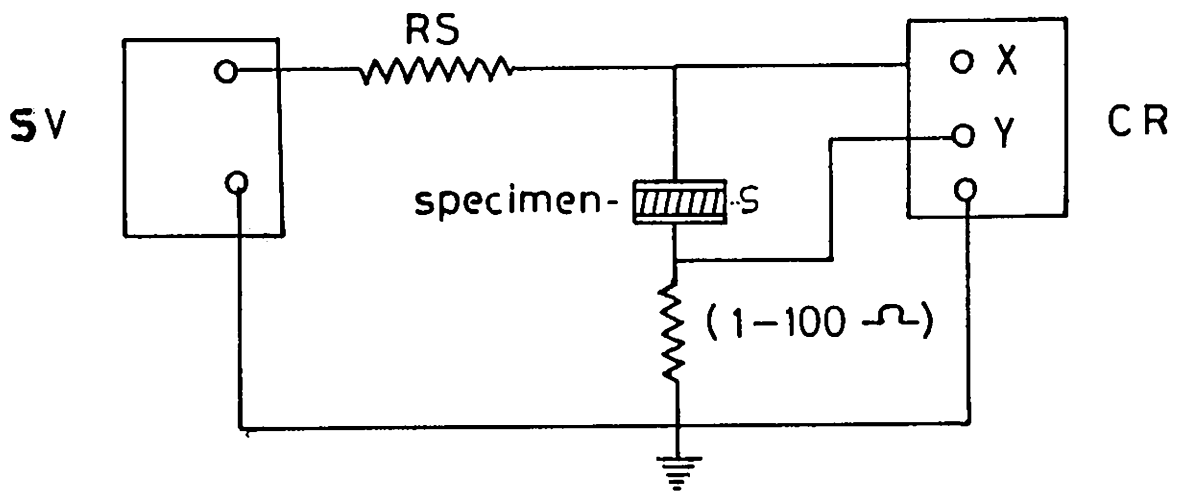
Fig.2.09    Schematic diagram of experimental set up
            SV - the sweep voltage source, RS - the series
            resistor, CR - the   XY   chart recorder,
            S - the specimen.

current and voltage across the specimen could also be
measured using digital multimeters in the automode or on an
X-Y chart recorder or a storage oscilloscope. Instead of
using a sweep voltage a pulse generator (ECIL, PG 707) may
be used. The switch ON and switch OFF pulses are initially
found out by trial method. For all the present studies, a
12 volt sweep voltage generator is used with current capability
of 250 milliamperes. After reaching the switching threshold,
current in the specimen would shoot up. The rise in the
current is limited by the series resistor to say 20 milliamperes
through the specimen  so that the specimen is protected from
damage. The specimen is set in the vacuum chamber and
electrical connections are made through shielded cables.

The capacitance versus voltage measurements are
carried out using a Hewlett packard LCZ bridge [4277A] and
the conductivity measurements by using an electrometer amplifier
[ECIL, EA 815]. By using this a current as low as $10^{-15}$ amperes
could be measured.

# REFERENCES

1. F.W.Billmayer, Text Book of Polymer Science, John Wiley and Sons, New York, 1970.

2. Anne Hiltner (ed.), Structure Property Relations of Polymeric Solids, Plenum Press, New York, 1981.

3. Daniel Klemprer and Kurt C.Frisch (ed.), Polymer Alloys, New York, Plenum Press, 1983.

4. C.K.Chiang, C.R.Fincher Jr., Y.W.Park, A.J.Heeger, H.Shrakawa, E.J.Louis, S.C.Gaus and A.G.Mac Diarmid, Phys. Rev.Lett. **39** (1977) 1098.

5. K.Yoshino, K.Tanimura, Y.Yamamota, K.Kaneto and Y.Inuishi, Technol.Reports, Osaka Univ., **28** (1978) 1430.

6. Hisashi Ueda, J.Polymer Sci.Pt.A. **27** (1989) 263.

7. Charles E.Carraher,Jr., John E.Sheats and Charles U. Pittman, Jr., Organometalic Polymers, Academic Press, New York, 1978.

8. J.M.Lupinski, K.D.Kopple and J.J.Hertz, J.Polym.Sci. **16** (1967) 1561.

9. S.Radhakrishnan and S.G.Joshi, J.Macromol.Sc. **B27** (1988) 291.

10. Raymond B.Seymour, Conductive Polymers, Plenum Press, New York, 1981.

11. H.Yasuda, Plasma Chemistry of Polymers, M.Shen (ed.), Marcel Dekker, New York, 1976.

12. Arthur Bradley and John P.Hammes, J.Electrochem.Soc. **110** (1963) 15.

13. M.Millard, Techniques and Applications of Plasma Chemistry, J.R.Hollahan and A.T.Bell (ed.), Wiley, New York, 1974.

14. M.Stolka, D.M.Pai, Advances in Polymer Science, Springer-Verlag, Heidelberg, 1978.

15. N.Karl, Fest Korper Problems, H.J.Queisser (ed.), Pergamon Press, New York, 1974, p.XIV.

16. P.H.Geil, E.Baer and Y.Wada, The Solid State of Polymers, Marcel Dekker Inc., New York, 1974.

17. Nirmala Paul, Ph.D.Thesis, Deptt. Physics, University of Cochin, India, 1981.

18. S.D.Phadke, Thin Solid Films, 55 (1978) 391.

19. K.L.Chopra, Thin Film Phenomena, McGraw-Hill Book Company, New York, 1979.

20. D.R.Lamb, Electrical Conduction Mechanism in Thin Insulating Films, Mathiuen and Co.Ltd., London, 1967.

21. John G.Simmons, Electronic Conduction through Thin Insulating Films, Handbook of Thin Film Technology, Leon I.Maessel and Reinhard G.Lang (ed.), McGraw Hill Book Company, New York, 1969.

22. H.Sasabe and S.Saito, J.Polym.Sci. **6A2** (1968) 1401.

23. Y.Osada, K.Yamada, I.Yoshizawa, Thin Solid Films, **151** (1987) 71.

24. A.Foss and W.Dannhauser, J.Appl.Polym.Sci. 7 (1963) 1015.

25. Keiichi Ando and Minoru Kusabiraki, Memoirs of the Faculty of Engineering, Osaka City Univ., 1978, p.19.

26. J.Chutia and K.Karua, Phys.Stat.Solidi (a) 55 (1979) K13.

27. N.F.Mott, Phil.Mag. **19** (1969) 835.

28. S.D.Phadeke, K.Sathianandan and R.N.Karekar, Thin Solid Films, **51** (1978) L9.

29. H.K.Henisch and J.A.Mayers, Thin Solid Films, **51** (1978) 265.

30. M.A.Lampert and P.Mark, Current Injection in Solids, Academic Press, New York, 1920.

31. A.Rose, Phys.Rev. **97** (1955) 1538.

32. D.F.Barbe and C.R.Westgate, J.Chem.Phys. **52** (1970) 4046.

33. Ya.M.Pushkin, T.P.Vrshnyakova, A.F.Lamin and S.A.Nizova, Organic Polymeric Semiconductors, D.Stutzkin (ed.), John Wiley & Sons, New York, 1974.

34. W.Gosling, A First Course in Applied Electronics, The Macmillan Press, 1975.

35. K.Mohanachandran, Ph.D.Thesis, Deptt. of Physics, University of Cochin, 1983.

36. O.Wiener, Wied.Ann. **31** (1987) 629.

# Chapter 3

## SWITCHING AND MEMORY IN PLASMA POLYMERISED

## POLYFURAN THIN FILMS

### Abstract

This chapter is presented mainly in two parts.
The first part describes switching behaviour of the plasma
polymerised polyfuran thin films carried out at the audio
frequency of 50 Hz. The preparation procedure and the setup
used for the audio frequency plasma polymerisation are
described. The growth rate and the structure are discussed.
The dependence of switching on the film thickness and temper-
ature is investigated. The activation energies in the ON and
OFF states are also evaluated. The second part describes the
preparation of polyfuran films by radio frequency (4.5 MHz)
plasma polymerisation. The dependence of $V_{th}$ on the film
thickness and temperature is also studied and compared to
polymer films prepared by audio frequency. From the investi-
gations, it is concluded that the mechanism of switching is
due to Poole-Frenkel effect followed by the formation of
conducting channels.

3.00   INTRODUCTION

Plasma polymerisation, eventhough not explored widely, holds potential scope for the preparation and modification of polymers [1]. They are used in a number of applications and are reported in the preceeding chapter. The properties of a polymer very much depend on the method of preparation [2]. This is due to the differences in the structures as the polymer is capable of existing in different molecular weights depending on the conditions of processing. The plasma polymerisation is a unique process for obtaining clean pinhole free polymer films. These films have very good adhesion, [3] mechanical strength and chemical stability. The method is effectively employed for the preparation of highly conducting [4, 5] ($10^4$ Ohm$^{-1}$cm$^{-1}$), semiconducting [6], and insulating films. This method is very useful for the introduction of metals into the polymer matrix [7, 8] by co-evoporation and plasma polymerisation. These metal-incorporated plasma polymers show many useful properties like high density laser beam memory, [8] catalytic effect and photochromic [9] behaviour.

In this chapter, preparation of plasma polymerised polyfuran thin films and their electrical studies are given. Switching studies are investigated for polyfuran thin films prepared by the audio frequency and radio frequency.

## 3.10    PREPARATION OF SILVER-POLYFURAN-SILVER SANDWICH

## STRUCTURES BY AUDIO FREQUENCY PLASMA POLYMERISATION

### 3.11    The plasma polymerisation chamber: Preparation of
Ag-PF-Ag structures.

The plasma polymerisation chamber is shown schematically

in Fig.3.01.   This consists mainly of three parts.   The pumping

module, the glow discharge chamber and the monomer feeding system.

The pumping module consists of a two inch diffusion pump D backed

by a 100 litres/min. rotary pump R., a liquid nitrogen trap LNT

and a baffle valve B.   The diaphragm valves $V_1$ and $V_2$ are used

for separately pumping glow discharge region (roughing) and the

diffusion pump region (backing) by the rotary pump R.   The dis-

charge chamber is isolated from the diffusion pump by means of

a water cooled baffle valve.   The upper flange of the baffle

valve is coupled to the base plate through which the monomer feed

through, power feed throughs, and pressure guage heads are

connected.   All the vacuum connections are made using   O-ring

seals.

The discharge chamber consists of a twelve inch bell-

jar 'G' which is coupled to the base plate using a neoprene

L-gasket.   Two metal electrodes $E_1$ and $E_2$ eighteen centimetres in

diameter are mounted on two vertical teflon rods.   The first elect-

rode is kept twenty centimetres above the base plate.   The other

electrode $E_2$ is parallel to $E_1$ and is three centimeters above

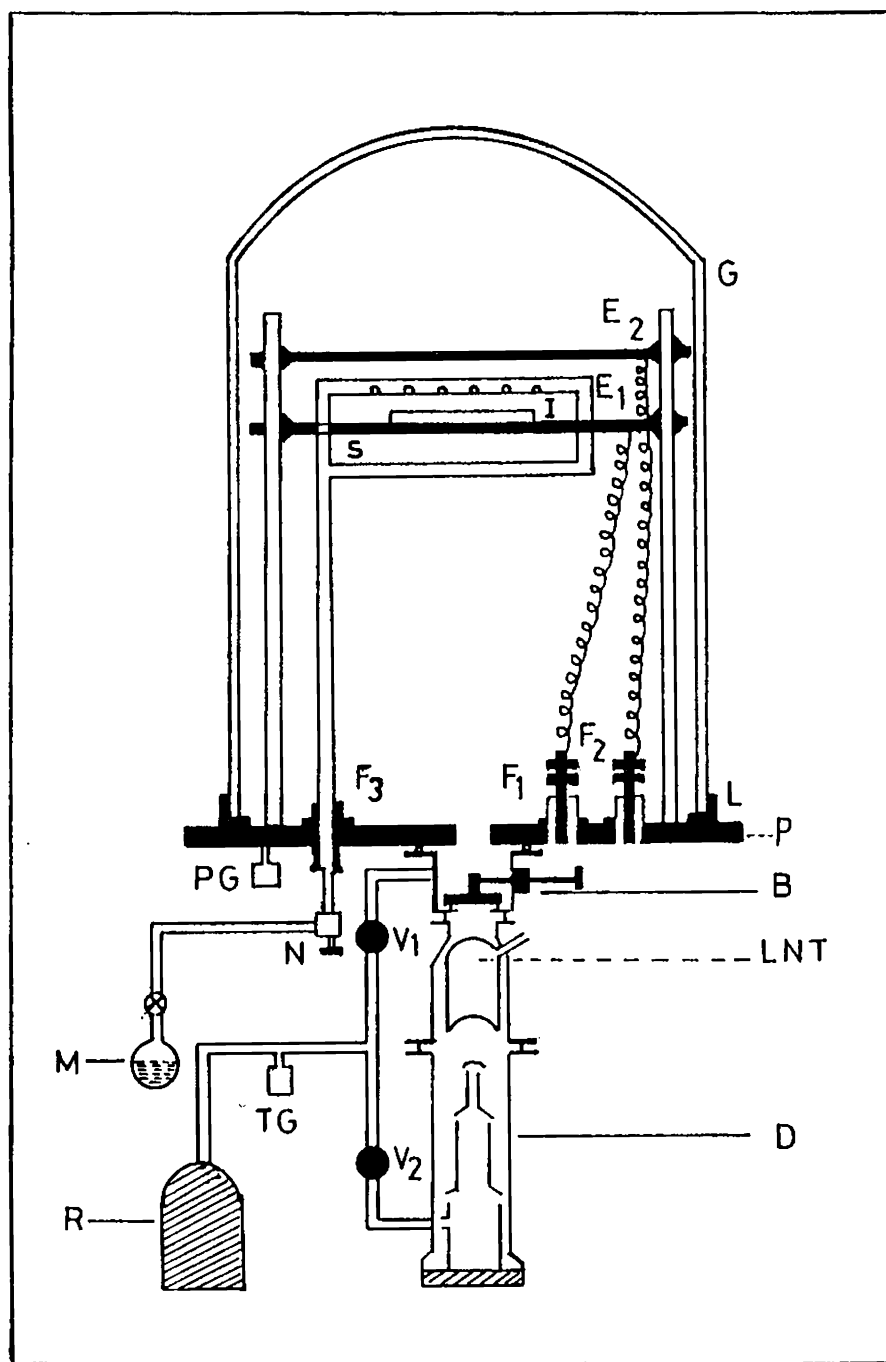$E_1$ as in Fig.3.01.   $E_1$ and $E_2$ are electrically isolated by the

Fig.3.01 Schematic diagram of plasma polymerisation chamber.
D - diffussion pump, LNT - liquid nitrogen trap,
B - baffle valve, R - rotary pump, $V_1$ - diaphram
valve for roughing, $V_2$-diaphragm valve for backing,
P - base plate, TG - thermo couple guage, PG - penn-
ing guage, G - bell jar, L - neoprene L gasket,
$E_1,E_2$ - plate electrodes, $F_1,F_2$ - high voltage
vacuum feed throughs, S - sprayer, I - substrate.

teflon supports using small nuts. Across these two electrodes a high voltage AC power supply is connected through two high voltage power feed throughs $F_1$ and $F_2$.

The high voltage power supply consists of 3 KV step up transformer with 150 milliamp. current rating. The primary voltage is controlled by a variac connected to the main. The secondary power is fed to the two electrodes through a series resistance ($1K\Omega, 10W$) and a milliammeter ($0-300$ mA). By controlling the primary voltage the discharge current can be adjusted for a steady glow. The monomer feeding system consists of a monomer container M with monomer furan, connected to a glass circular sprayer S through a needle valve N and a feed through $F_3$. The sprayer gives a uniform distribution of monomer vapours between the electrodes.

The plasma polymerisation takes place at moderate pressures of the order of less than one torr. The pumping is made in the following sequence. The baffle valve is closed tightly and the diffusion chamber is pumped down to $10^{-2}$ torr through $V_2$ using the rotary pump. Subsequently, the chamber is pumped to $10^{-2}$ torr including the monomer path through valve $V_1$. After attaining rotary vacuum, $V_1$ is closed and $V_2$ is opened facilitating pumping through $V_2$ and diffusion pump. Now the diffusion pump is operated keeping the baffle valve

open and water cooled. The chamber is pumped down to $10^{-4}$ torr

allowing the diffusion pump operating with backing pump in

series. The pressure is read from the penning gauge. Now the

baffle valve B and $V_2$ are closed and the system is pumped

through $V_1$. The monomer container stop cock is opened through

the control needle valve for an appropriate discharge pressure

say 0.6 torr. The voltage across the electrodes is increased

and the plasma current is set for a current density of 0.1 milli-

amp/cm$^2$ at 400-425 volts. A steady glow discharge is maintained.

Under these conditions, the polymer formation can be noticed

on the electrodes. Chemically and ultrasonically cleaned glass

substrates with suitable silver electrodes are used. The

electrode is made by vacuum coating of silver to masked glass

substrates. These substrates with electrodes are placed on the

lower electrode of the plasma chamber. A proper mask allows

coating of polymer over a suitable area of the electrode.

After obtaining a polymer thickness of 500-1000Å, silver counter

electrode is coated to form one square centimetre area of

silver-polyfuran-silver sandwich structure. The so prepared

Ag-PF-Ag structure is subjected to electrical switching studies

by using the experimental setup described in chapter 2.


3.12  Growth rate of the polymer

        The growth rate of plasma polymer depends on the

amount of monomer molecules and the plasma current. Since the

polymerisation takes place at moderate pressure, the amount

of monomer molecule is proportional to the effective pressure

inside the polymerisation chamber. The plasma current is again

dependent on the amount of molecules present and the applied

voltage across the electrodes. There is a threshold value of

voltage for the initiation of the plasma discharge. This again

depends on the inter electrode spacing and monomer pressure.

To study the growth rate of the polyfuran films,

the films are prepared on clean substrates for various intervals

of time. The time of polymerisation is varied by keeping constant

the monomer pressure (0.6 torr) and the discharge current

(20 milliamps). The inter electrode spacing is kept three

centimetres. Initially the discharge is carried out for ten

minutes. The thickness of the polymer film formed is measured

using Fizeau fringes. The polymerisation is carried out for

twenty minutes, thirty minutes and so on upto one hour on

separate substrates.

The growth rate of polymer with time is as shown in

Fig.3.02. After about fifty minutes the growth rate is found

to be slow. This is due to the insulative effect of the polymer

films. The growth rate is proportional to the plasma current

as ·seen from the-Fig.(3.02). As the polymer grows the plasma

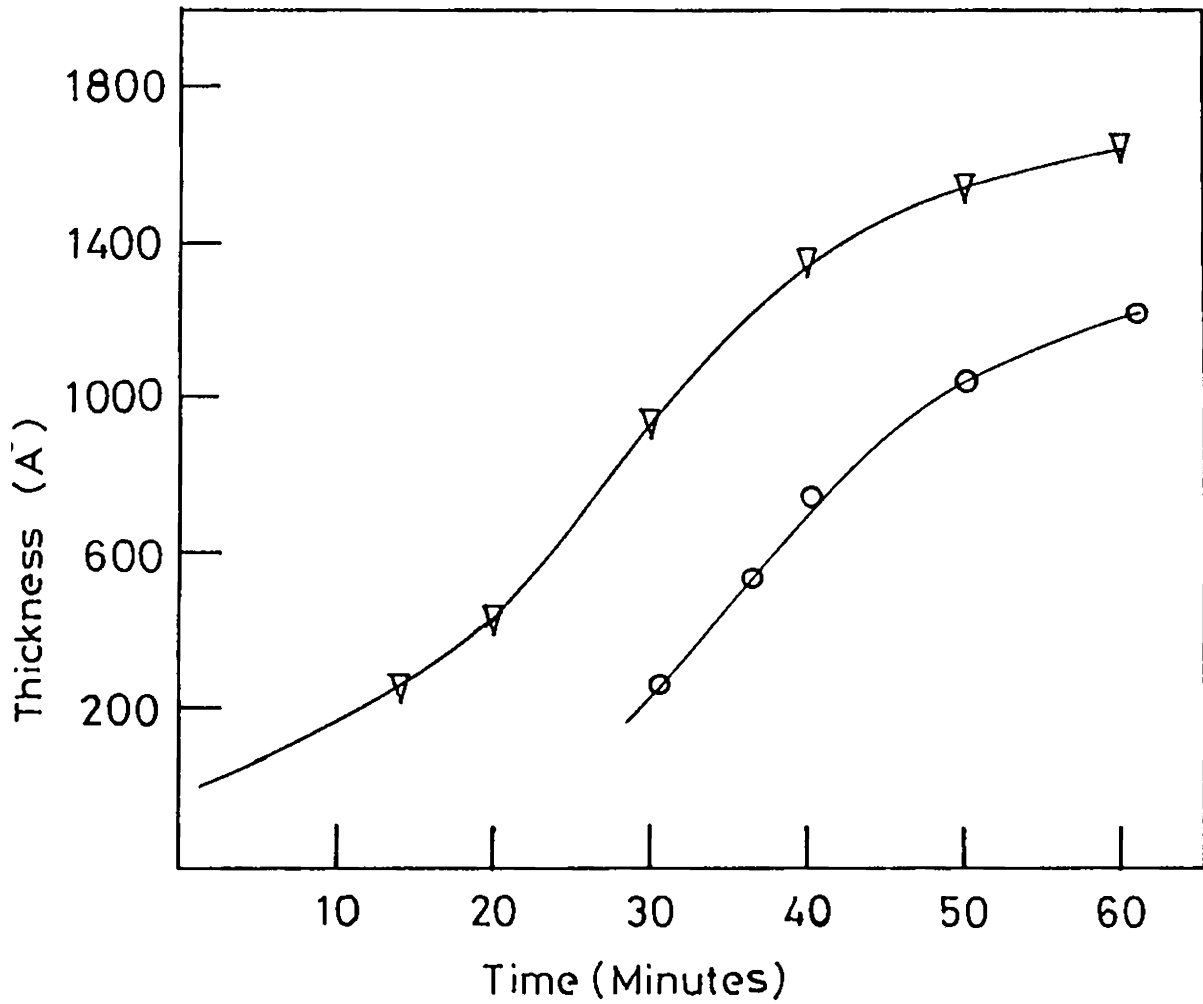current also will decrease. After a few trials, it is possible

Fig.3.02  The growth rate of audio frequency prepared plasma
polyfuran films for two different plasma current
densities  —△—20 mA/cm$^2$, —O—10 mA/cm$^2$ ; Thickness
in Angstrom units and time in minutes.

to optimize the conditions for the preparation of polyfuran films. If the power exceeds the optimum value, arcing would take place resulting in the poor formation of polymer films on the substrates with uneven surface textures. Excess of monomer pressure also will lead to poor discharge. So these parameters are fixed to appropriate values by a few preliminary experiments.

The growth rate is proportional to the power transferred to the monomer molecules and hence the ionisation. The ions and electrons are accelarated towards the electrodes. These accelerated ions and electrons collide with other monomer molecules and the energy is transferred by the impact. Radicals are formed by these impacts. These radicals then combine to form a polymer molecule. The growth rate depends on this radical formation and their combining rate to form a polymer. The possible general structures of polyfuran with defects are as shown in Fig.3.03.

3.13 The current-voltage characteristics of Ag-PF-Ag structure: switching behaviour.

Fresh samples of Silver-Polyfuran-Silver structures of plasma polymerised thin films are kept in the electrical chamber and subjected to current-voltage characteristic studies as described in the experimental setup earlier. Silver is found to be a good ohmic contact to the film for lower fields. The
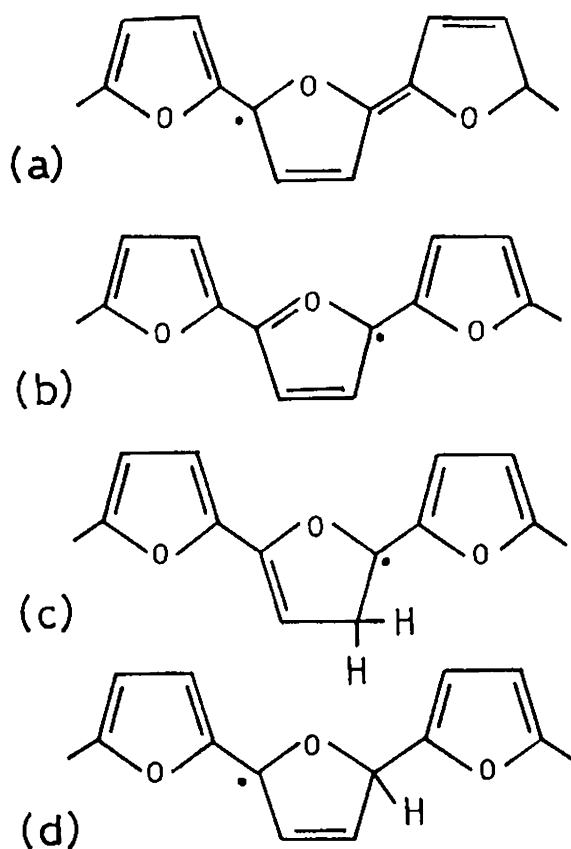
Fig.3.03  The possible structures of polyfuran films
with defects.
(a) bond alteration, (b) • – radical induced
by removal of proton and in (c) & (d) radical
induced by addition of proton.

films are annealed at $100^\circ C$ in vacuum $(10^{-2})$ for an hour.

For fresh films a forming process is found to occur as described

by Chopra [10] and Simmons [11]. On increasing the sweep voltage

at the rate of 0.5 V/minute, the current rose from $10^{-9}$ amps to

$10^{-3}$ amps as shown in Fig.3.04 at a particular threshold voltage

$V_{th}$ and above. The first current rise is always at a higher

threshold voltage but for the subsequent switching events a

lower threshold voltage is found to be sufficient. The switched

film showed a non volatile memory at zero bias. Initially the

impedance of the film was high (OFF-State) and after switching

the resistance became a few tens of ohms (ON-State). The two **imped-**

**ances states were** stable for long durations. A change from the

ON state to the OFF state took place on the application of a

pulse voltage of sufficient power. This process of breakdown

is thus regenerative and the ON-OFF commutation is possible for

several hundred times. The films are found to switch in air

medium also.


3.20   RESULTS AND DISCUSSION

3.21   Effect of film thickness on the switching threshold.

The dependence of switching threshold voltage on the

film thickness is investigated for $700\overset{o}{A}$ to $1800\overset{o}{A}$ and is illust-

rated in Fig.3.05. A linear dependence of switching threshold

is noticed with the thickness. This gives a switching threshold

field of $2.12 \times 10^6$ V/cm. For lower thicknesses, $(< 700\overset{o}{A})$ the
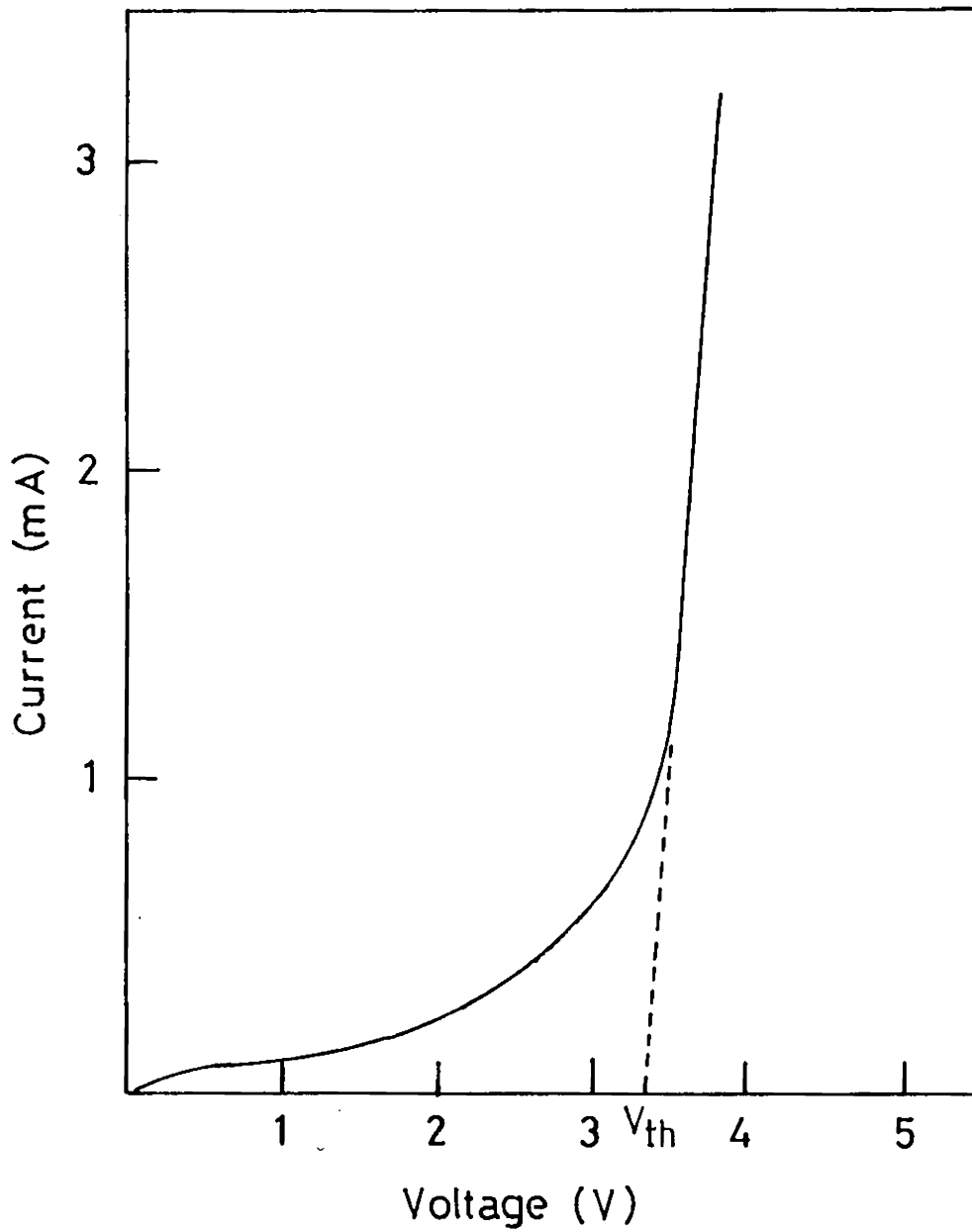
Fig.3.04   The current voltage switching characteristic of
           Ag-PF-Ag structure.   Film thickness 1220Å
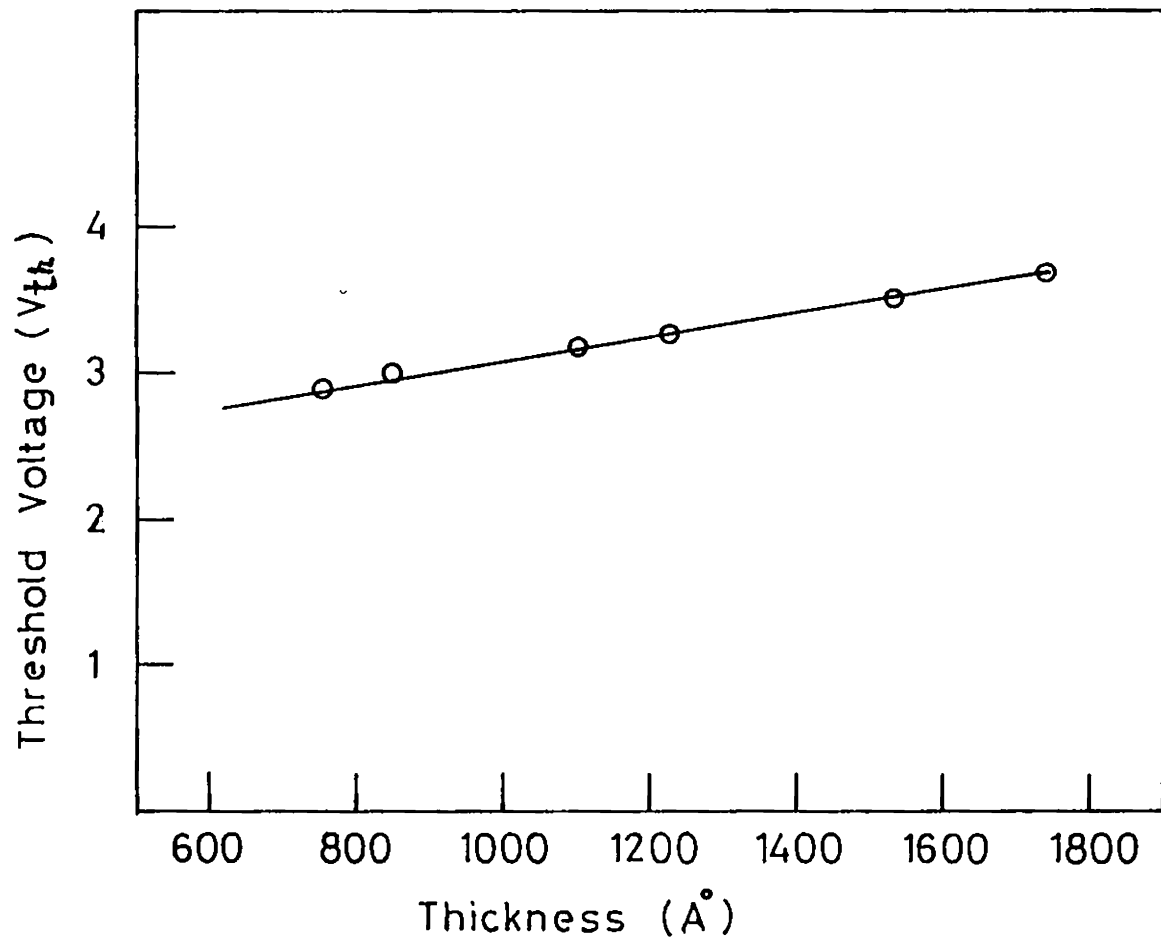           ($V_{th}$) the threshold voltage.

Fig.3.05   Dependence of threshold voltage $V_{th}$ on film thickness.

films are found to short very easily. For higher thicknesses ( $>1800\overset{o}{A}$ ) the forming and switching is difficult.

## 3.22 Dependence of threshold voltage on film temperature

The dependence of $V_{th}$ on the film temperature for the range 298K to 383K is as shown in Fig.3.06. The switching threshold is found to decrease with the increase of film temperature. The decrease is more pronounced at higher temperatures. The temperature coefficient of resistance (TCR) is positive in the OFF state and is $5x10^{-4}K^{-1}$ for the formed film as shown in Fig.3.07. The TCR in the ON state is negligible compared to that of silver. Hence the formation of metallic bridge is ruled out.

## 3.23 Discussion

For a polymer according to Segui et al. [ 12 ] a transition from an amorphous state to a more long range ordered state would never give the conductivity reported here. Hence an order disorder mechanism is not a favoured process for the observed switching in this polymer.

From the analysis of the I-V characteristic, it is found that ohmic conduction takes place for lower fields. The $\ell nI$ vs. $V^{\frac{1}{2}}$ plot (Fig.3.08) for the fields in the range of
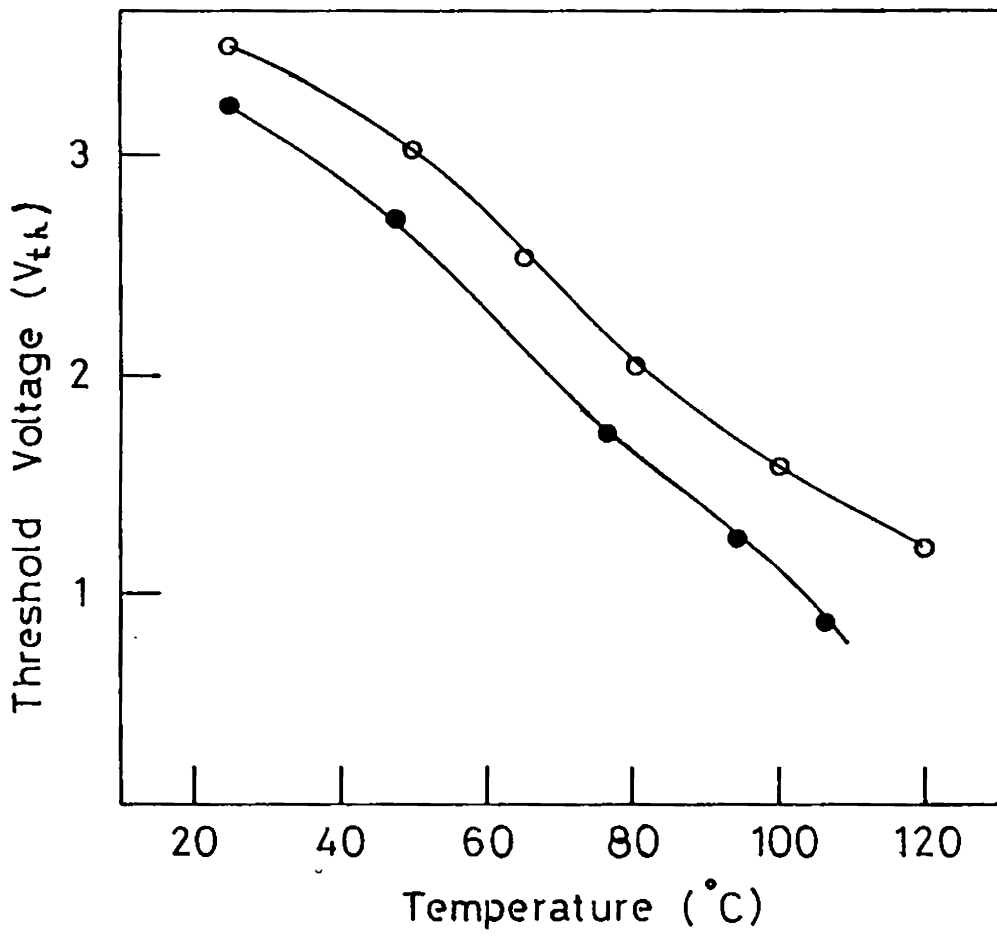
Fig.3.06   Dependence of threshold voltage $V_{th}$ on threshold
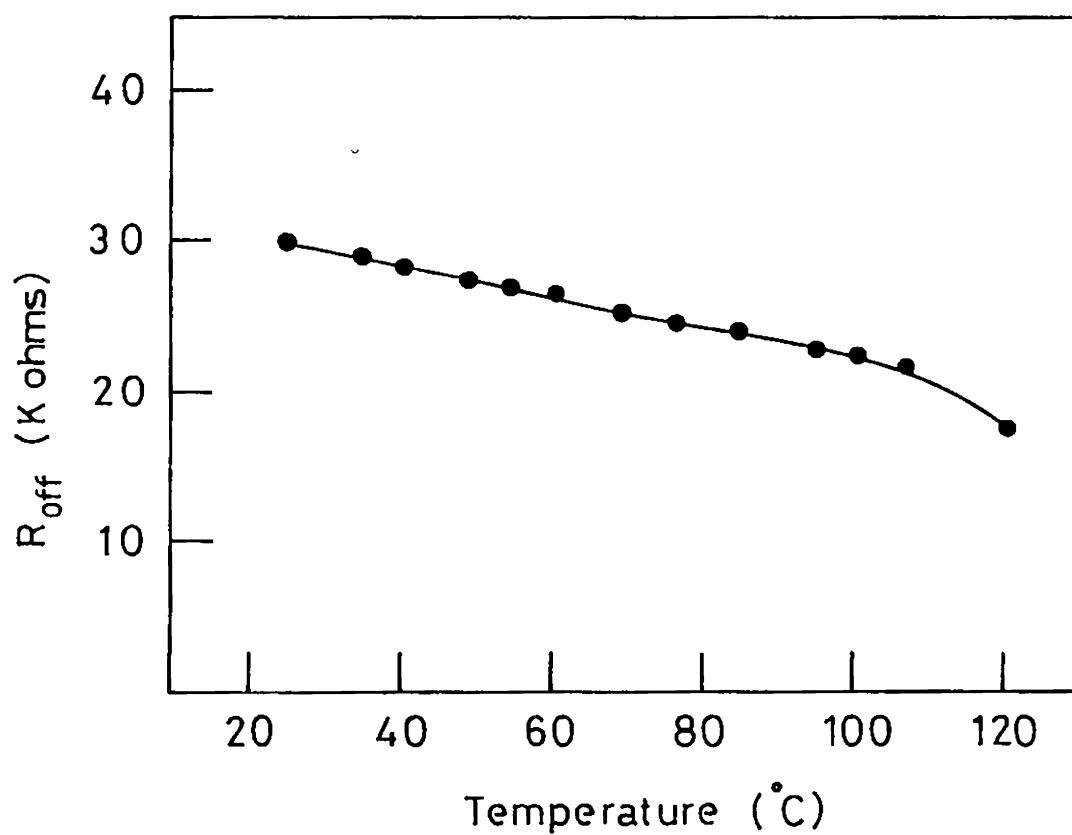for two film thicknesses –O–1536Å and –●–1200Å.

Fig.3.07  The variation of OFF state resistance with film
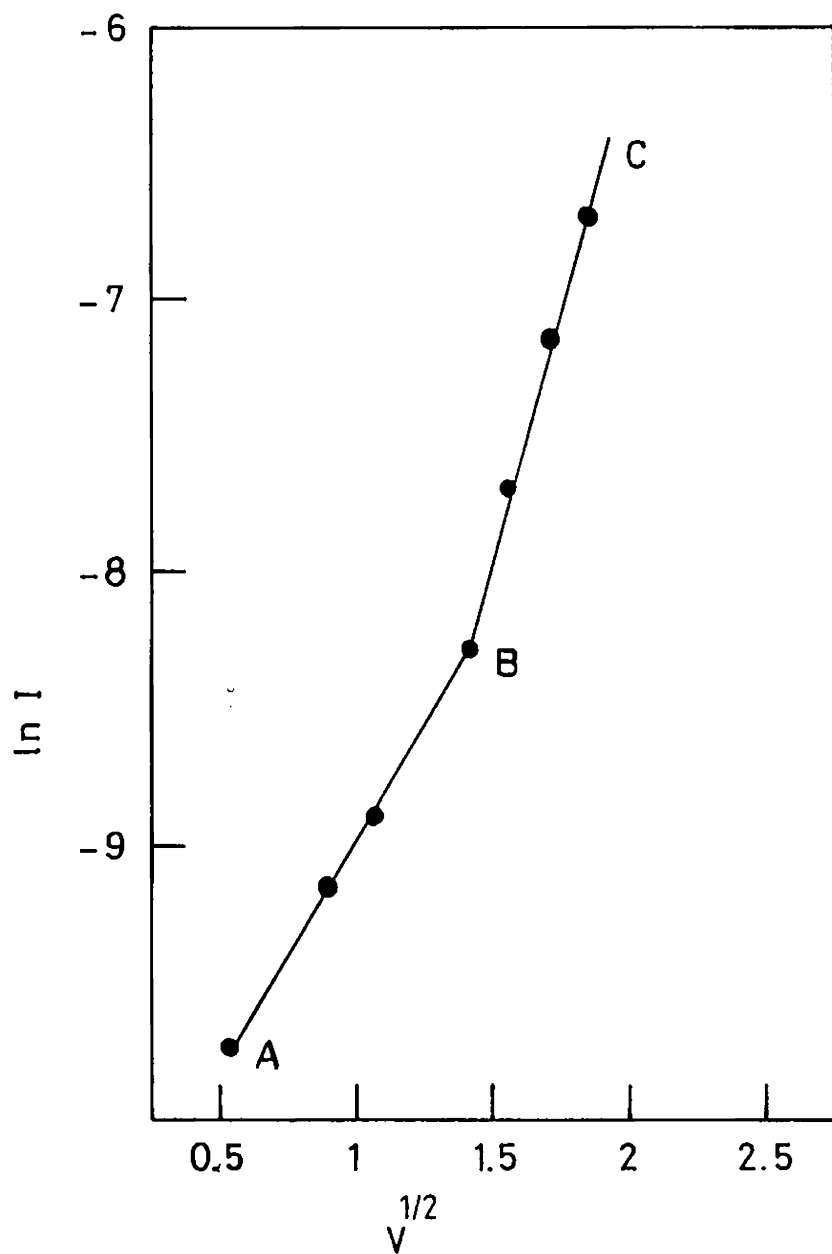temperature.  Thickness 1536Å.  TCR = 5 x $10^{-4}K^{-1}$.

Fig.3.08    𝑙nI versus V$^{1/2}$ plot for polyfuran films.  The region AB with slope 1.6 shows Poole-Frenkel conduction, BC is the switched region.

$5.74 \times 10^3$V/cm to $1.15 \times 10^5$V/cm. yields a straight line with a slope of 1.6. This suggests that either Poole-Frenkel or Schottky conduction takes place. From the $\ln I$ versus $\ln V$ plot (Fig.3.09) also the presence of Poole-Frenkel or Schottky conduction is confirmed. This is observed for lower fields and is evident in the region with slope 1/2. Using electrodes of dissimilar work functions, that is with Silver-Polymer-Aluminium configuration, the I-V characteristic is found to be symmetric for both the polarities. Hence the conduction mechanism is a bulk phenomenon and is Poole-Frenkel. If it were Schottky mechanism which is an electrode limited process, this would have reflected when the electrode materials with different work functions were used.

The trap density would be high due to the amorphous nature of the polymer which leads to such a mechanism. Reviews relating the switching on amorphous materials are given by Drake [13], Tauc [14] and Ray and Hogarth [15]. Thermally assisted detrapping could take place. But the temperature dependent threshold voltage and the high activation energy (Fig.3.10) rules out purely electronic mechanism for switching. The observed temperature dependence of $V_{th}$ is characteristic of thermo electronic mechanism [16] in which conducting channels are formed. This is supported by the fact that the change of electrode area does not affect the threshold voltage and more-over the very high OFF resistance (greater than 20 M ohm) and
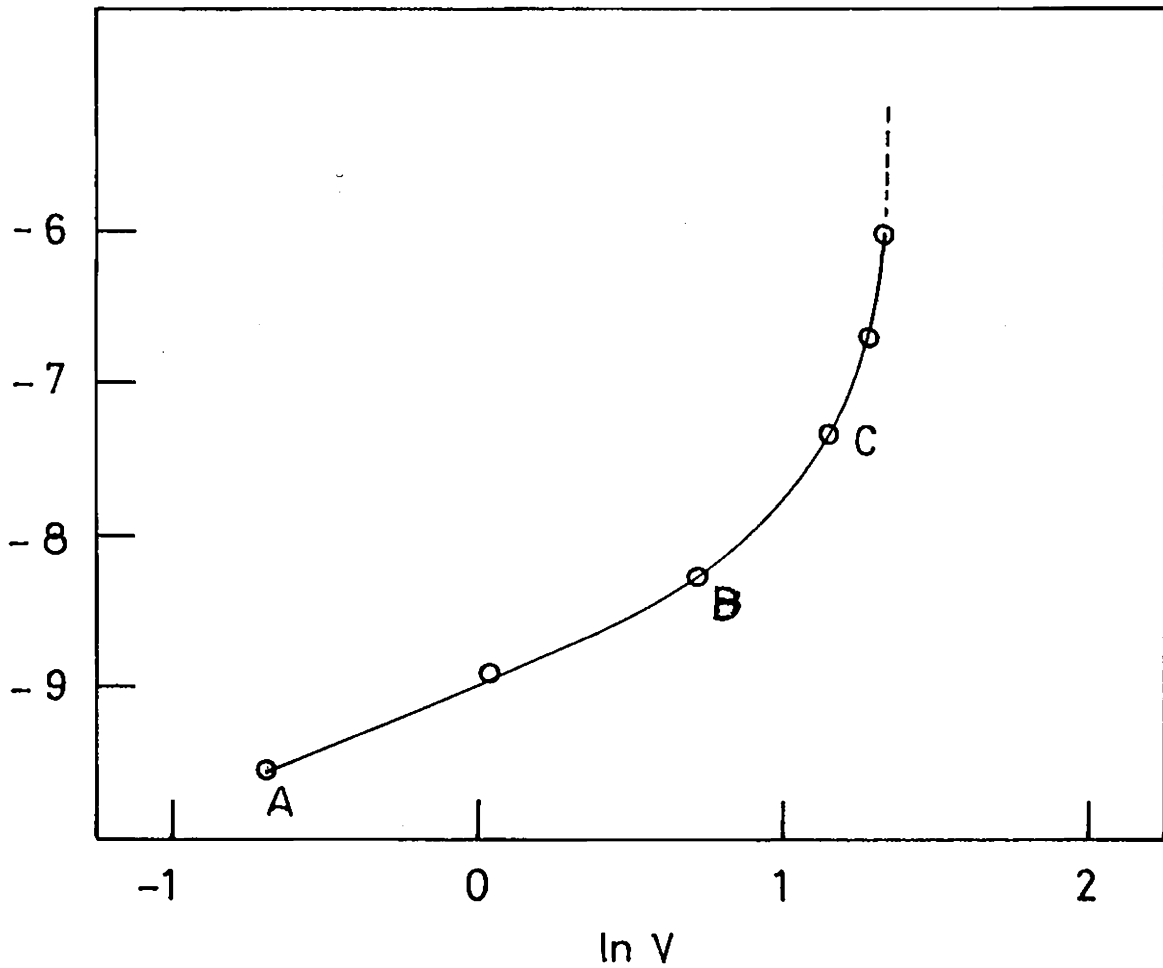
Fig.3.09  $\ell$nI vs. $\ell$nV plot for Ag-PF-Ag structure.  The region
AB with slope ½ shows Poole-Frenkel conduction region.
Film thickness 1740Å .

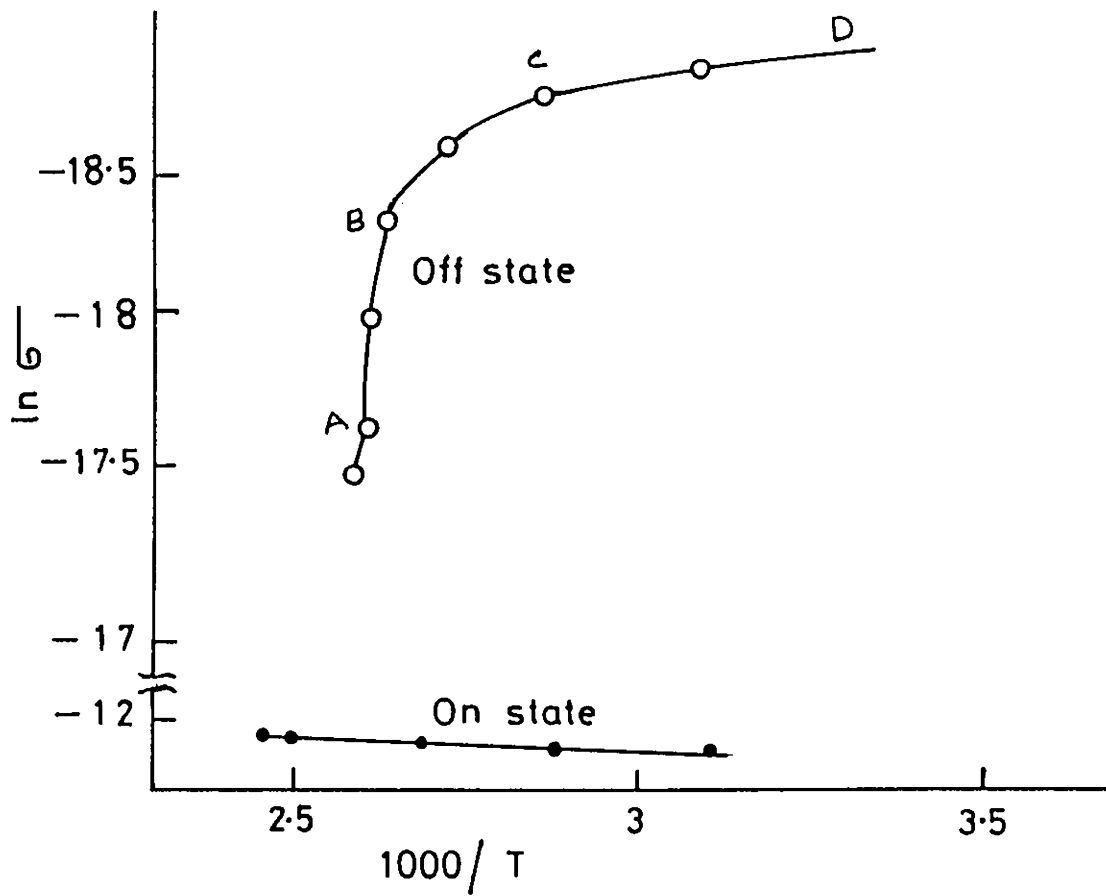Fig.3.10 ℓn.σ versus 1000/T plot for ON and OFF states. Film thickness 1536Å. The OFF state activation energy is 1.55 ev, slope AB = 17.39 and slope CD = 0.5.

low ON state resistance (10-40 Ohms) support filament formation. The observed variation of ON state resistance for different cycles of switching can be attributed to the variations in the number and size of the conducting channels [17] taking part. The channel formation shows a negative capacitance and is actually observed. The application of a suitable pulse causes sufficient temperature rise to rupture the conducting channels resulting the device reverting to high impedance state. The switching cycles are finite as this mechanism is not sufficient for a stable and durable behaviour. The channel formation is a final stage of switching. Electronic mechanism prior to channel formation is evident where the resistance of film is comparatively low.

3.30    PREPARATION OF POLYFURAN FILMS BY RADIO FREQUENCY PLASMA
        POLYMERISATION

        The preparation procedure of the radio frequency plasma polymerisation is carried out using the same system of audio frequency polymerisation unit. Instead of the 50 Hz line frequency source is used. The source is a 4.5 MHz Ozcillator. All other procedures of preparation of the metal polymer metal sandwich configuration are the same as used for the audio frequency glow discharge.

The radio frequency polymerisation may also be carried out by feeding the power externally. The electrical power may be transferred to the plasma by inductive or capacitive method. In this case, a plasma tube of pyrex or quartz is used. The inductive and capacitive coupling methods are shown in Fig.3.11(a) and (b). In the case of inductive coupling an inductive coil is used to couple the power. In the case of capacitive coupling two copper foil rings are used and kept apart. The deposition will be in the glow discharge region (Fig.3.11(c) and (d)). The substrate kept in the glow discharge region, gets the polymer coating to the desired area by proper masking. The main advantage of RF discharge is that due to external coupling the discharge region will be comparatively free of any other impurity. The RF discharge is also based on free radical polymerisation in which breaking of covalent bonds takes place followed by a recombination to form the polymer.

3.31   The growth of the RF polyfuran films

The growth rate of the radio frequency plasma polymerisation is also dependent on the amount of monomer molecules, the optimum pressure for discharge and the discharge current flowing through it. Being very high frequency, the power transferred to the molecules will be greater and hence the growth
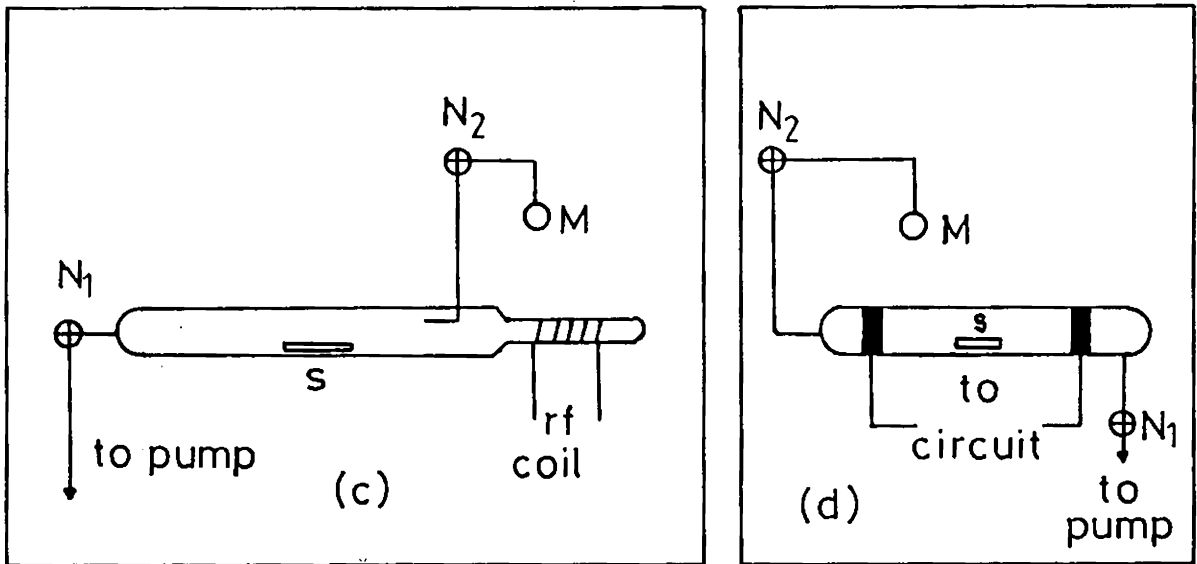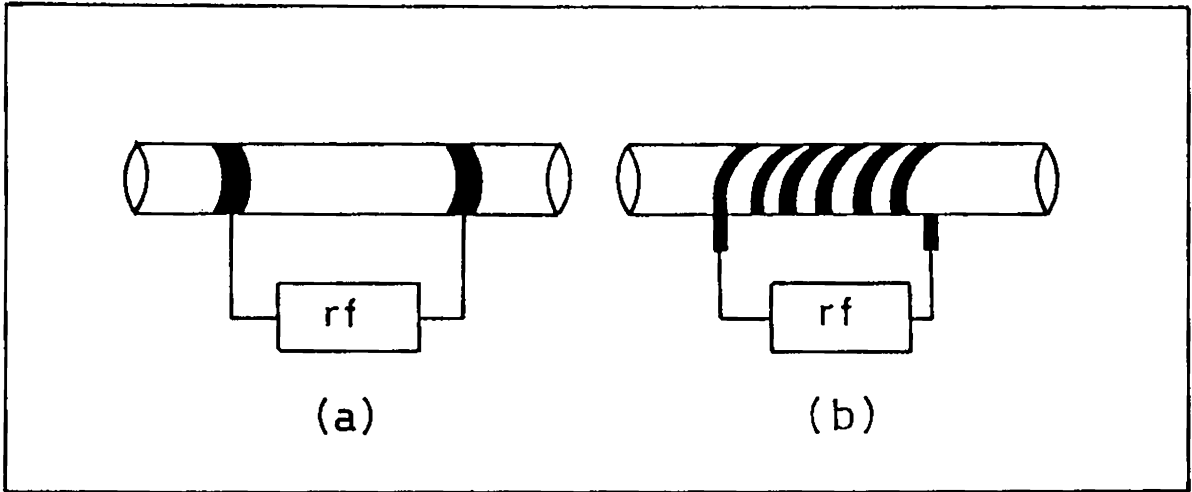
Fig.3.11 (a) The capacitive coupling of radio frequency power.
(b) The inductive coupling of RF power.
(c) The schematic representation of inductive coupled plasma polymerisation reactor, $N_1$- stop cock, $N_2$ - needle valve, M - monomer and S - substrate.
(d) The schematic representation of capacitive coupled plasma polymerisation reactor.

rate is very much higher than the 50 Hz A.C. discharge. This is evident from the Fig.3.12. The polymerisation is carried out for different times and the thicknesses are found out by the Fizeau method. The discharge current is kept constant at 20 milliampere.

### 3.32 Effect of film thickness and temperature on the switching threshold $V_{th}$

The dependence of switching threshold voltage on the film thickness was investigated for the range 600$\overset{o}{A}$ to 1200$\overset{o}{A}$. A linear dependence of switching threshold voltage with thickness is obtained 9 (Fig.3.13). The threshold field is found to be $3.2 \times 10^5$ V/cm. The dependence of threshold voltage on the film temperature is investigated. The threshold voltage is found to decrease as in the case of plasma films prepared by audio-frequency. This is as shown in Fig.3.14.

### 3.40 DISCUSSION AND COMPARISON OF SWITCHING SHOWN BY AF AND RF FILMS

The switching in the radiofrequency plasma prepared polyfuran films is also due to the conducting filamental formation as in the case of polymer films prepared by audio frequency. In both the cases, the dependence of $V_{th}$ on film thickness and temperature are alike. In this case also the
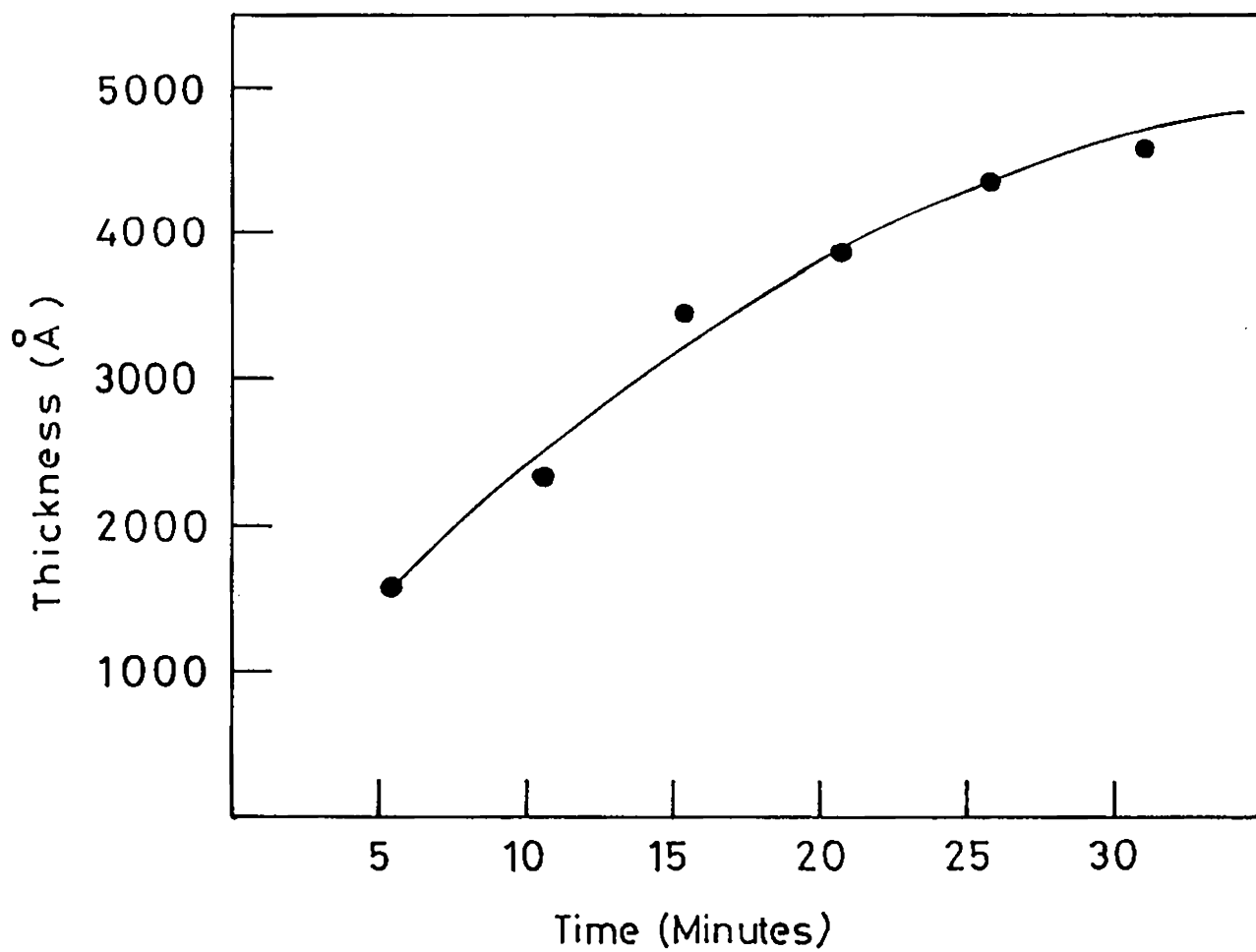
Fig.3.12   Growth of radio frequency polyfuran films with time
          for 0.1 mA/cm$^2$ current density  thickness in Angstram
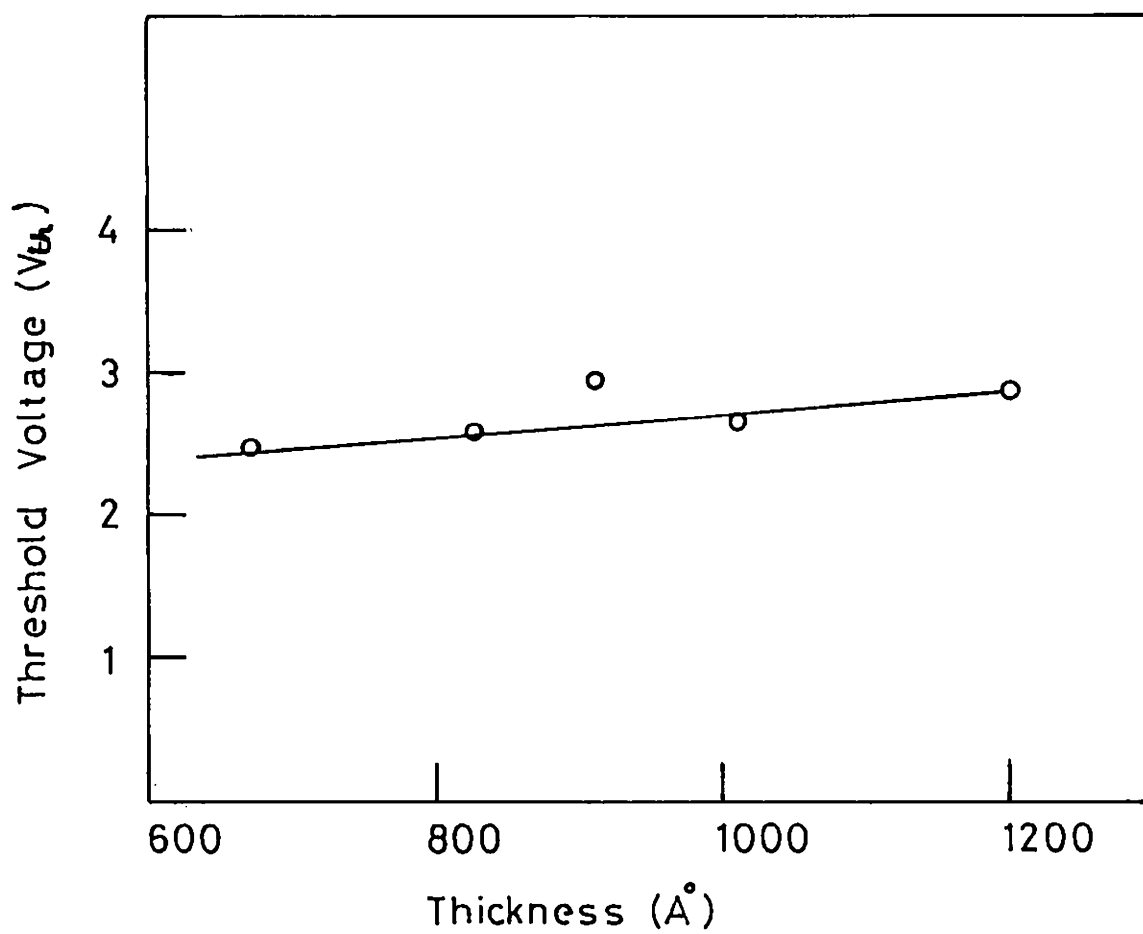          units.

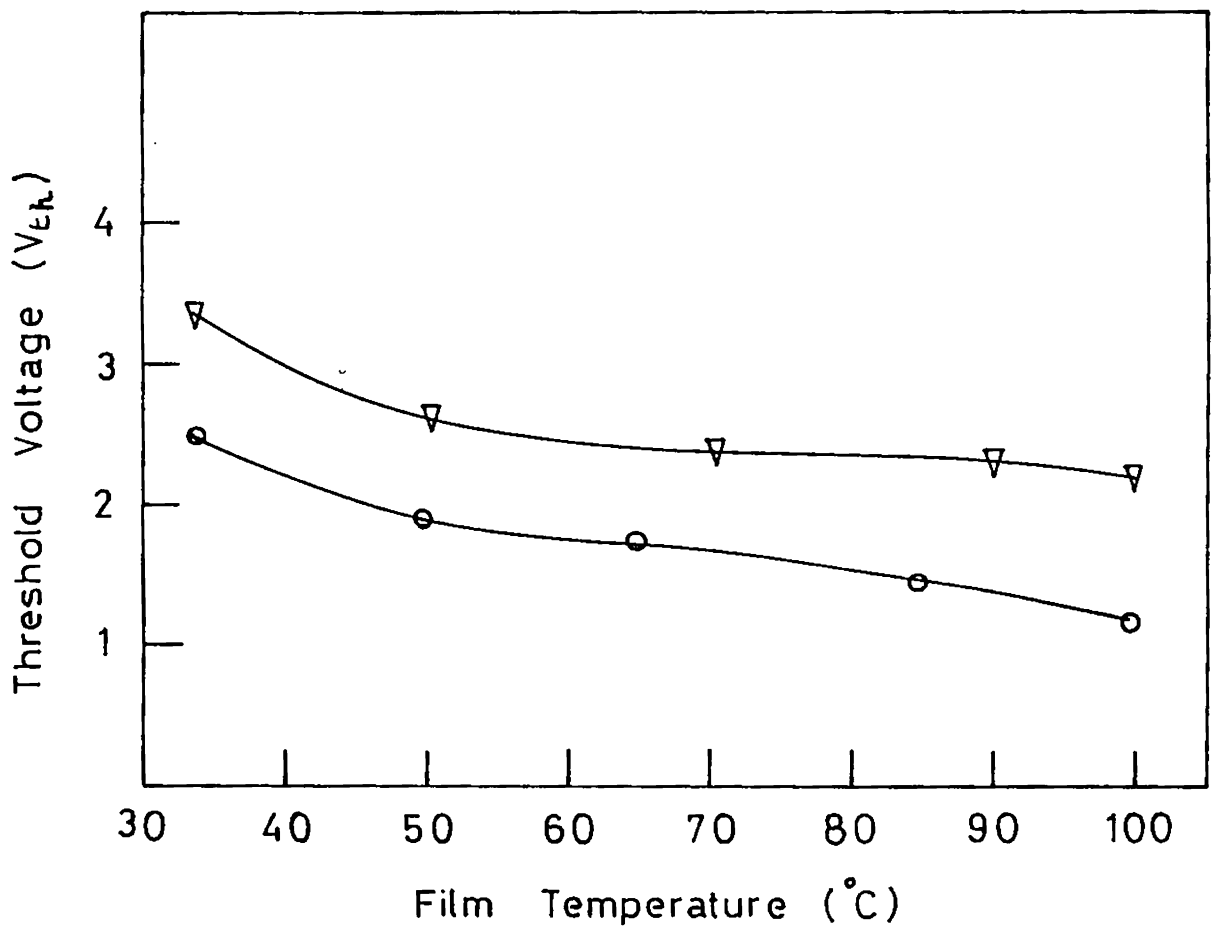Fig.3.13   Effect of film thickness on threshold voltage ($V_{th}$) for (RF) polyfuran films.

Fig.3.14  Variation of $V_{th}$ with film temperature for (RF)
polyfuran switches.  Film thickness,$\triangle$-1620Å, 0-800Å.

current path is filamental because as in the case of audio

frequency film, there is no dependence of current to area of

the film. Negative capacitance is found in this case also.

A decrease of threshold field of about one order is found in

the case of radio frequency plasma polymer films. This may

be due to the decrease in density of traps 'N' and imperfect-

ions possible for the polymers prepared by the radio frequency

discharge. In the case of AF films, it is $2.12 \times 10^6$ V/cm and

in the case of RF films it is $3.2 \times 10^5$ V/cm. The external

adsorbate effects are also less prominent in the case of RF

films. This is supported by the smooth dependence of threshold

voltage on the film temperature compared to that of

AF films. The growth rate of the polymer is very high in the

case of radio frequency polymer films. This is as expected.

At higher frequencies the energy transfer to the molecules

will be greater and hence higher polymerisation rate. For

the case of RF polyfuran films the dielectric constant measured

for various films is found to be 2.2 and the dielectric break-

down field is found to be $2.5 \times 10^6$ V/cm and is in agreement with

the laser damage studies conducted on these films in our

laboratory. The I-V characteristic is similar in both cases.

In both types of films Poole-Frenkel emission of carriers

take place and the switching is due to the conducting filament

formation. Eventhough the general behaviour is the same, the

differences observed can only be due to the difference in the molecular weight, cross linking, the number of traps present and the impurity concentration.

# REFERENCES

1. H.Yasuda, Thin Film Process, J.Vossen and W.Kern (eds.), Academic Press, New York, 1979.

2. Harold Suhr, Techniques and Application of Plasma Chemistry, John R.Hollahan and Alexis T.Bell (ed.), John Wiley and Sons, New York, 1974, Ch.II, p.57.

3. B.V.Tkachuk, Yu.D.Kobtsev, E.P.Laurs, V.I.Mikhal chen and N.Ya.Marusshi, IZV vyssh Uchebn Zaved, Fiz. 15 (1972) 117.

4. R.K.Sadhir and W.J.James, Thin Solid Films, 97 (1982) 17.

5. W.J.James and Li Pei Tseng, J.Vac.Sci.Technol. A36 (1985) 2425.

6. E.Kny, W.J.James, L.L.Levenson and R.A.Auerbach, Thin Solid Films, 85 (1981) 23.

7. Y.Asano, Thin Solid Films, 105 (1983) 1.

8. A.Mizumoto and Y.Osada, J.Appl.Phys. 59 (1986) 1776.

9. Y.Osada, Y.Tsuruta, A.Mizumoto, K.Shigehara, A.Yamada, J.Macromol.Sci.Chem. A24 (1987) 403.

10. K.L.Chopra, J.Appl.Phys. 36 (1965) 184.

11. J.G.Simmons, J.Phys.D. 4 (1971) 613.

12. Y.Segui, Bui Ai, and H.Carchano, J.Appl.Phys. **47** (1976) 140.

13. C.F.Drake, Thin Solid Films, **50** (1978) 125.

14. J.Jauc, Phys.Today, October 1976, 23.

15. A.K.Ray and C.A.Hogarth, Int.J.Electron. **57** (1984) 1.

16. J.Swiatek, Thin Solid Films, **41** (1977) 5.

17. R.Vogel, Appl.Phys.Lett. **14** (1969) 216.

# Chapter 4

## SWITCHING AND MEMORY IN THIN POLYACRYLONITRILE FILMS

### Abstract

This chapter presents the switching investigations on polymerised acrylonitrile thin films (PAN) using audio frequency and direct current discharges. The methods of film preparation are briefly described. The preparation of transparent conducting tin oxide films is also presented. The dependence of switching threshold voltage on PAN film temperature and thickness is given. The investigations of temperature coefficient of resistance, the activation energy, the dependence of threshold voltage on film temperature and thickness, and the analysis of current voltage characteristic show that the mechanism of switching is due to electronic origin in both audio frequency and direct current discharge prepared films.

126

4.00   INTRODUCTION

The search for stable switching in polymer films necessiated the investigation in different polymers.   The initial switching behaviour observed in our laboratory on poly-acrylonitrile films prepared by plasma polymerisation motivated a detailed study on switching in this polymer.   Polyacrylonitrile is an 'electret' with good charge storage capability possessing polar nature with a-CN side group [1].   Detailed theoretical and experimental results on the charge storage mechanism are given by Van Turnhout [2].   Eventhough bistable switching is reported in the case of evaporated PAN [3], the phenomenon is not investigated in the same polymer obtained by other methods.   It is well known that the properties of a ploymer depend on the method of preparation.   The relaxation time of permanent dipoles and space charges are widely distributed in this polymer [4].   Though the role of dipole in switching is not clear, the space charges play a major role in the bistable switching in this polymer.

4.10   SWITCHING IN AUDIO FREQUENCY PLASMA POLYMERISED
          POLYACRYLONITRILE THIN FILMS

4.11   Preparation of polyacrylonitrile films by audio frequency
          plasma polymerisation and experimental details.

The general preparation procedure of polyacrylonitrile thin films by plasma polymerisation is the same as that described in chapter 3.   Chemically and ultrasonically cleaned glass

substrates are suitably masked and aluminium electrodes of

1500 Å thick are evaporated on to it to form the lower electrode.

The electrode coated substrate is again masked so that polymer

is formed at the desired portion of the electrodes. These are

then placed in the plasma polymerisation set up as described

previously. The monomer acrylonitrile is taken in the monomer

container. The electrodes are kept at a distance of three

centimetres apart. The polymerisation chamber is flushed well

with the monomer vapour. The polymerisation is carried out at

a constant monomer pressure of 0.6 torr with a current density

of 0.1 milliamp/$cm^2$ at 400 to 425 volts, at 50 Hz. A steady

plasma is sustained between the electrodes forming the polymer

deposit on the electrodes on the glass substrate. The growth

rate is shown in Fig.4.01. As the insulator thickness increases

the growth rate is found to decrease. The possible structures

of the PAN as the film grows, are isotactic placement or

syndiotactic placement [5] (Fig.4.02). But the structures of

the plasma polymers would be having many defects and variations

from the ideal possible structure. The polymer coated specimens

are transferred to the electrode coating unit. Silver counter

electrode is evaporated to the specimens to form one square

centimetre of metal-polymer-metal sandwich structure. The

sample is kept in the metal vacuum chamber with electrical

connections and is evacuated to $10^{-2}$ torr. The current voltage

characteristic is then plotted by using an X-Y chart recorder.
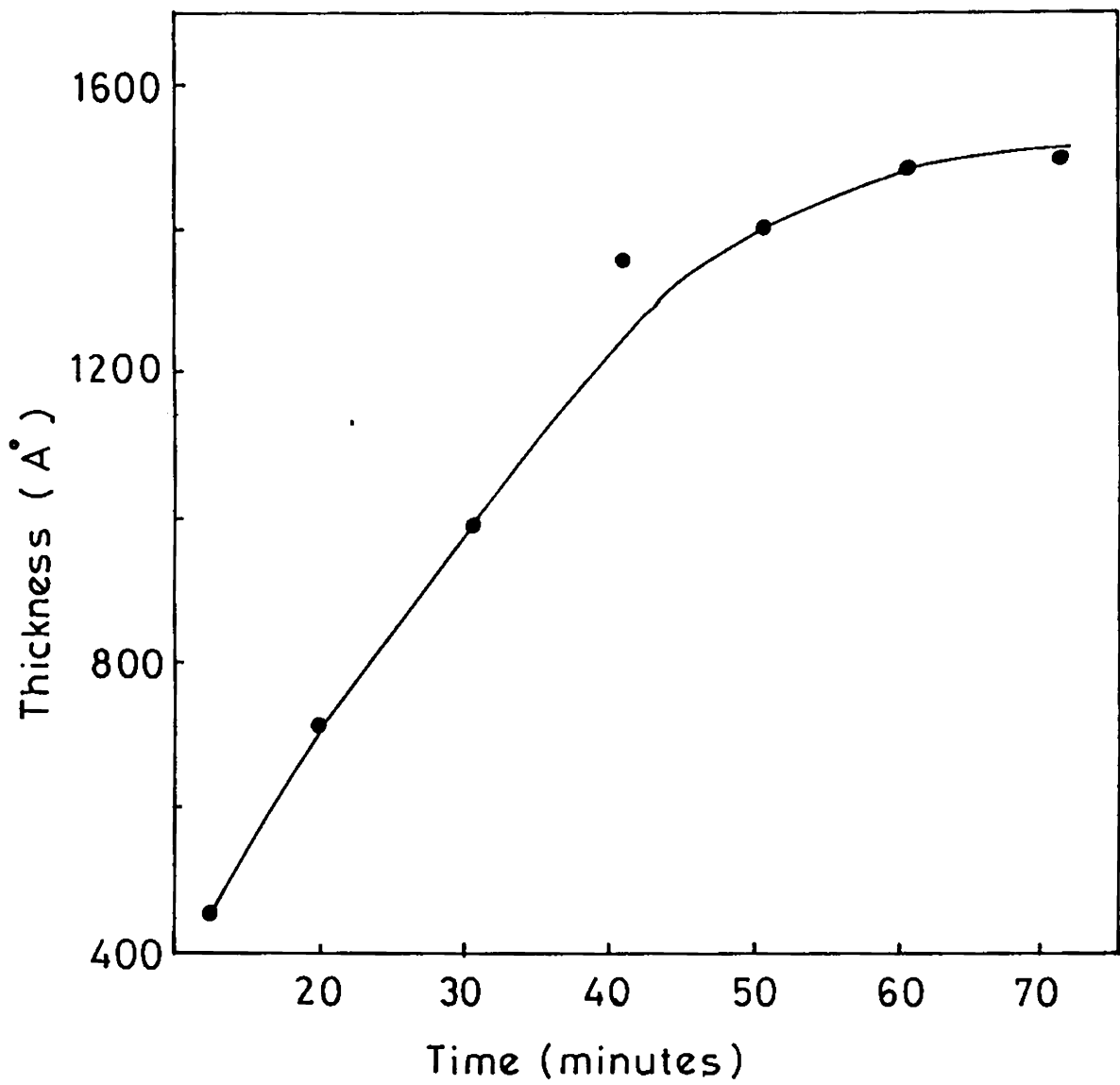
Fig.4.01    Growth rate of polyacrylonitrile films
            (PAN  AF  polymerised) current density
            0.1 mA/cm$^2$ at 0.6 torr vacuum.
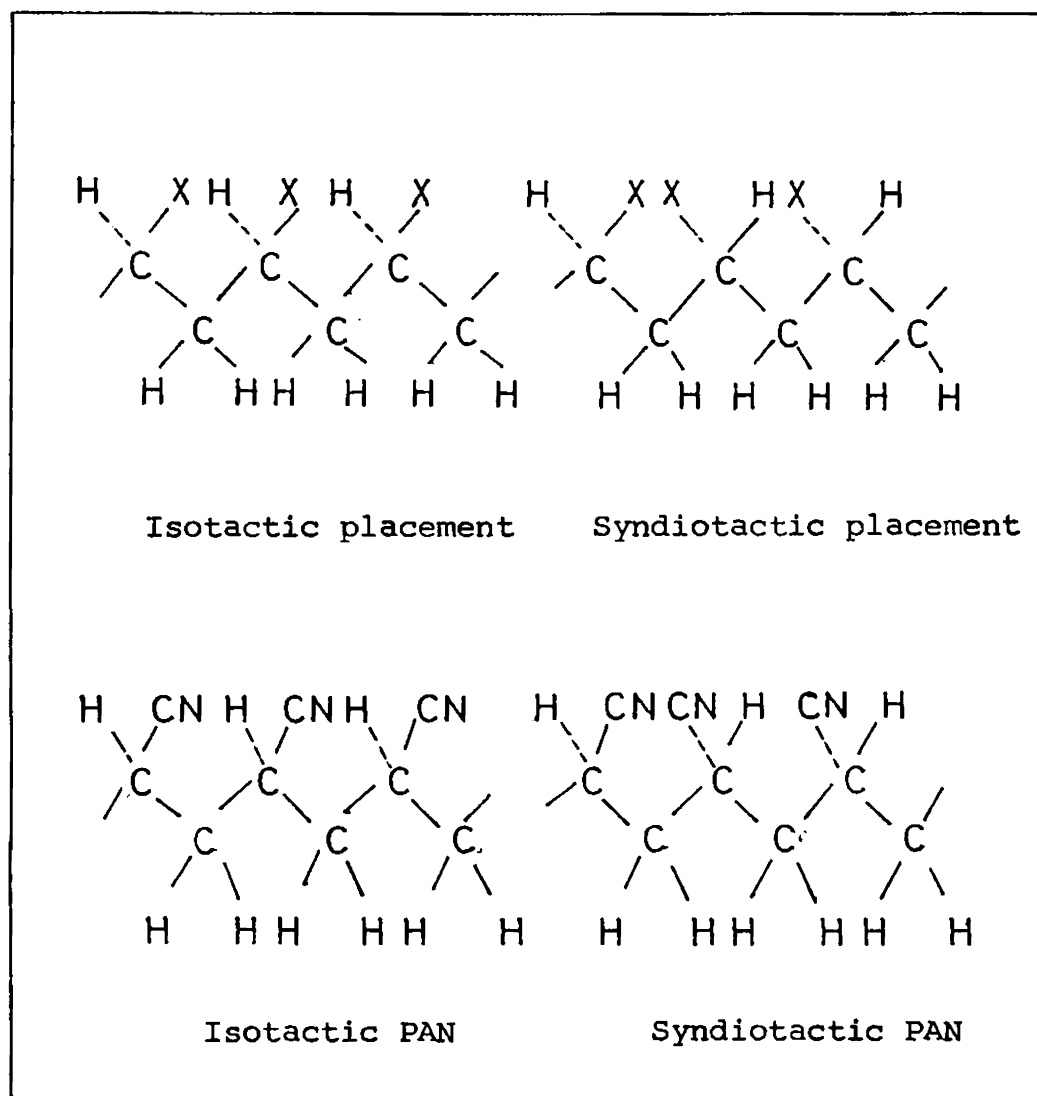
Fig.4.02   The probable structures of plasma polymerised
          PAN films.   Isotactic placement and syndiotactic
          placement are shown.

The voltage is linearly increased at the rate of 0.5 V/minute using the sweep voltage generator. A series resistance of 100 Ohm is connected with the film to limit the current through the film. A pulse generator is also used for applying suitable pulses to switch OFF or ON the film.

## 4.12 Spray pyrolysis for conducting transparent electrodes

The simultaneous occurrence of high optical transparency in the visible region and high electrical conductivity are not possible in an intrinsic stoichiometric material. Partial transparencies and fairly good conductivity may be obtained in thin films of a variety of metals. But nonstoichiometric and doped films of oxides of tin, Indium, Cadmium, Zinc and their alloys deposited by various techniques exhibit high transmittance in the visible region, high reflectance in the IR region and nearly metallic conductivity. The most prominent ones are the oxides of indium and tin doped with appropriate dopants. These transparent conductors have found major applications in a vast number of active and passive electronic and optoelectronic devices as resistors, transparent heating elements for air craft windows, heat reflecting mirrors in glass windows and incandescent bulbs, antireflection coating, electrodes to liquid crystals, electrochromic and feroelectric photoconductors, storage and display devices, selective absorber components in solar heat collectors, gas sensors, touch sensitive switches and solar cells [6].

Extensive work on transparent conducting films are carried out on their preparation and characterisation [7,8]. Since electrical and optical transport of these films depend strongly on their stoichiometry and the nature of impurities present, each deposition techniques with its associated parameters often yields films of different properties. The films have been prepared by almost all thin film depositing techniques such as oxidation of metal, reactive evaporation, thermal evaporation, electron beam evaporation, sputtering, reactive ion plating, chemical vapour deposition, chemical solution growth and spray pyrolysis [9].

The present method of preparation of transparent electrodes is by spray pyrolysis. This method allows high quality film with high transmittance and low resistivity. The method employs a very simple experimental set up. Spray pyrolysis involves spraying a solution usually aqueous, cont-containing soluble salts of the constituent atoms of the desired compound on to a heated substrate. The important control parameters are the nature and temperature of the substrate, the solution composition, the gas solution flow rates, the desorption time and the nozzle to substrate distance. In the present case, a number of trials were made to optimise these parameters.

The glass plate to be coated was first thoroughly cleaned by detergent, chromic acid, and distilled water. It was then placed on a hot plate made of thick stainless steel which can be heated up to 450°C. The spray solution was prepared using $SnCl_2.5H_2O$ saturated in isopropyl alcohol. The spray was produced by blowing compressed air into the sprayer and was controlled by adjusting the valve. Spraying is done such that it hits the hot substrate at 450°C. The substrate to nozzle distance was about 30 cms. The films prepared under these conditions show a sheet resistance of 80 ohm/cm$^2$ and transmittance of about 85 per cent. In order to make the desired electrode width, $SnO_2$ is selectively etched by using nascent hydrogen produced by zinc dust and hydrochloric acid. These films showed good adhesion to the substrates.

4.13 Observations of switching in PAN films

Polyacrylonitrile thin films prepared by plasma polymerisation showed bistable switching. On increasing the sweep voltage at the rate of 0.5 V/minute the current rose suddenly at a particular threshold voltage as shown in Fig.4.03. For fresh films a forming process is found to occur. The first current rise is at a higher threshold value for pre-formed films. But for the subsequent switching events, a lower threshold voltage is sufficient for the switching to
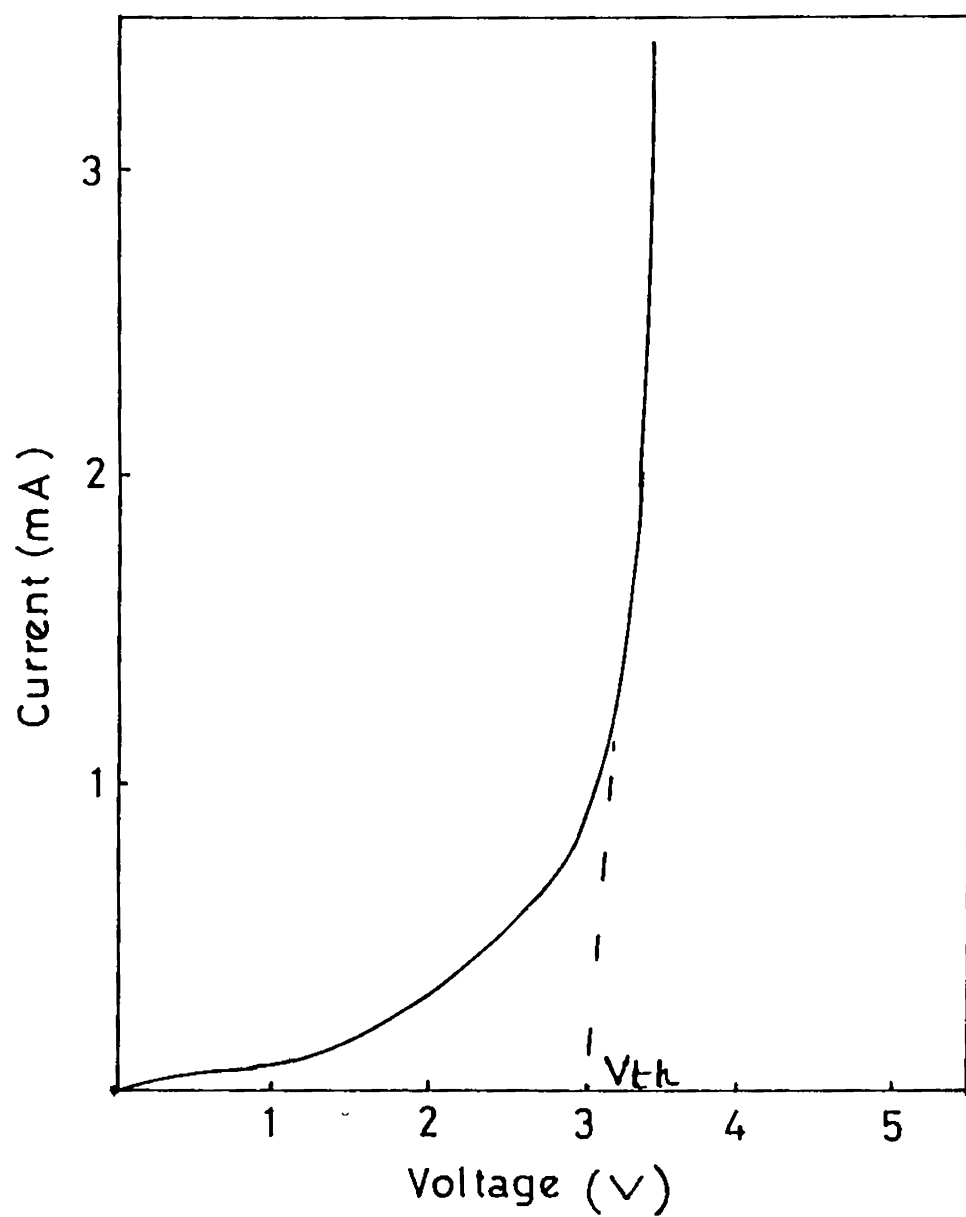
Fig.4.03 The switching characteristic of AF polyacrylo-
nitrile film: sweep voltage rate 0.5 V/minute,
film thickness 550Å, $V_{th}$ - threshold voltage.

take place. A resistance change of three to four orders is observed for these films. The two impedance states are by and large stable for many months. When the current through the specimen is made larger, a low ON state resistance ($\sim$ 300 Ohm) is attained. On leaving the film free, the ON state resistance is found to increase exponentially to Kilo Ohms region as shown in Fig.4.04. The ON-OFF commutation is possible for large number of events. The switching time is found to be less than $0.1\mu$ s. Approximately 10% variation of threshold voltage is found to occur for large number of switching events. A three order capacitance change is observed from OFF state to ON state (nano to pico farads) as in Fig.4.05. Different electrode assemblies of silver, aluminium, tin oxide, mercury are found to exhibit switching in polyacrylonitrile thin films.

In order to observe directly the switched film, transparent conducting electrodes are used. The transparent conducting electrode of tin oxide are prepared by spray pyrolysis described earlier. The polymer film is deposited over this tin oxide film. This specimen is dipped in mercury in a beaker so that the mercury forms counter electrode. Switching is carried out in this structure. The switching is reproducible with this structure for a large number of events. The specimen after many switching events is observed through
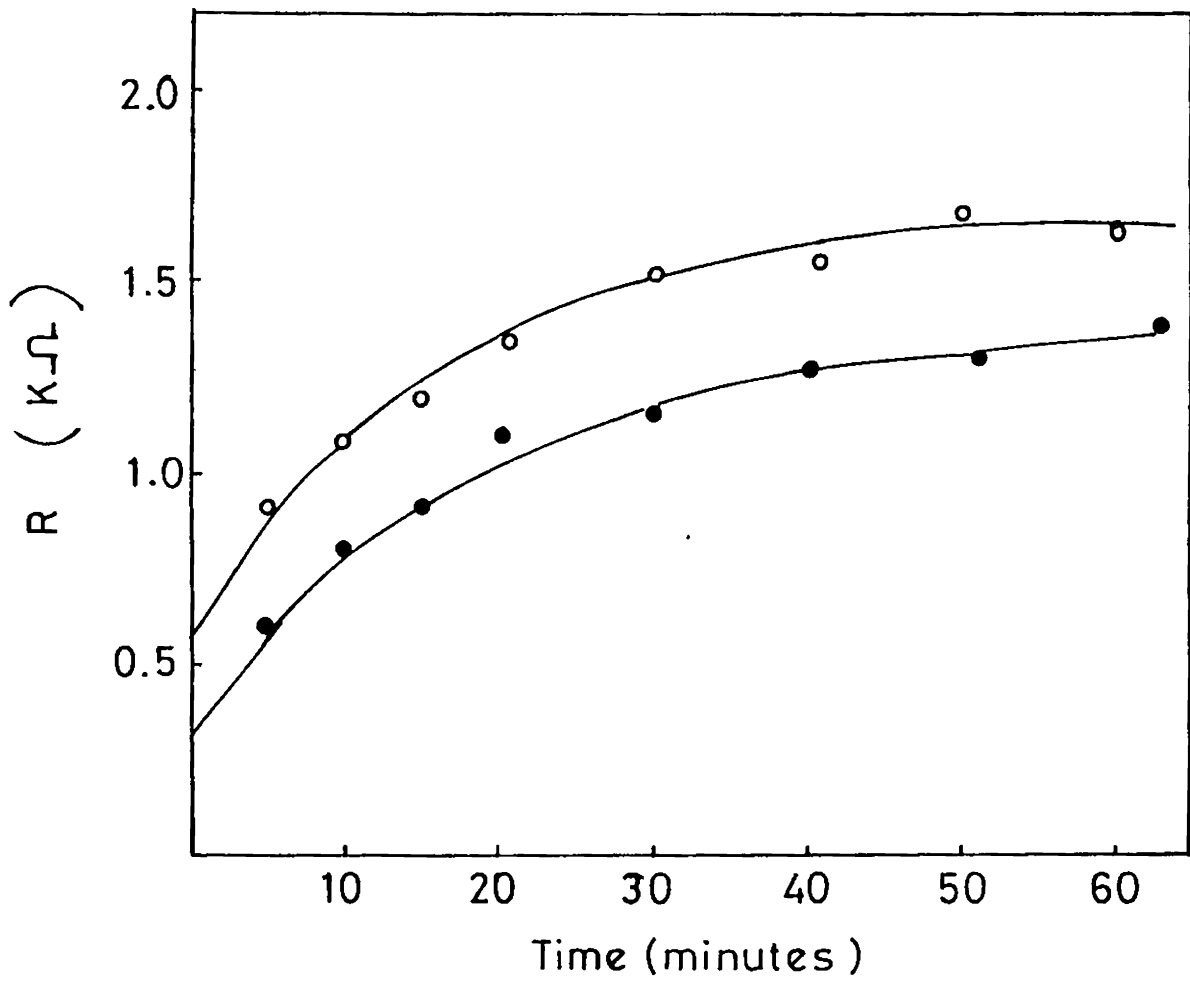
Fig.4.04   The variation of ON state resistance with time for
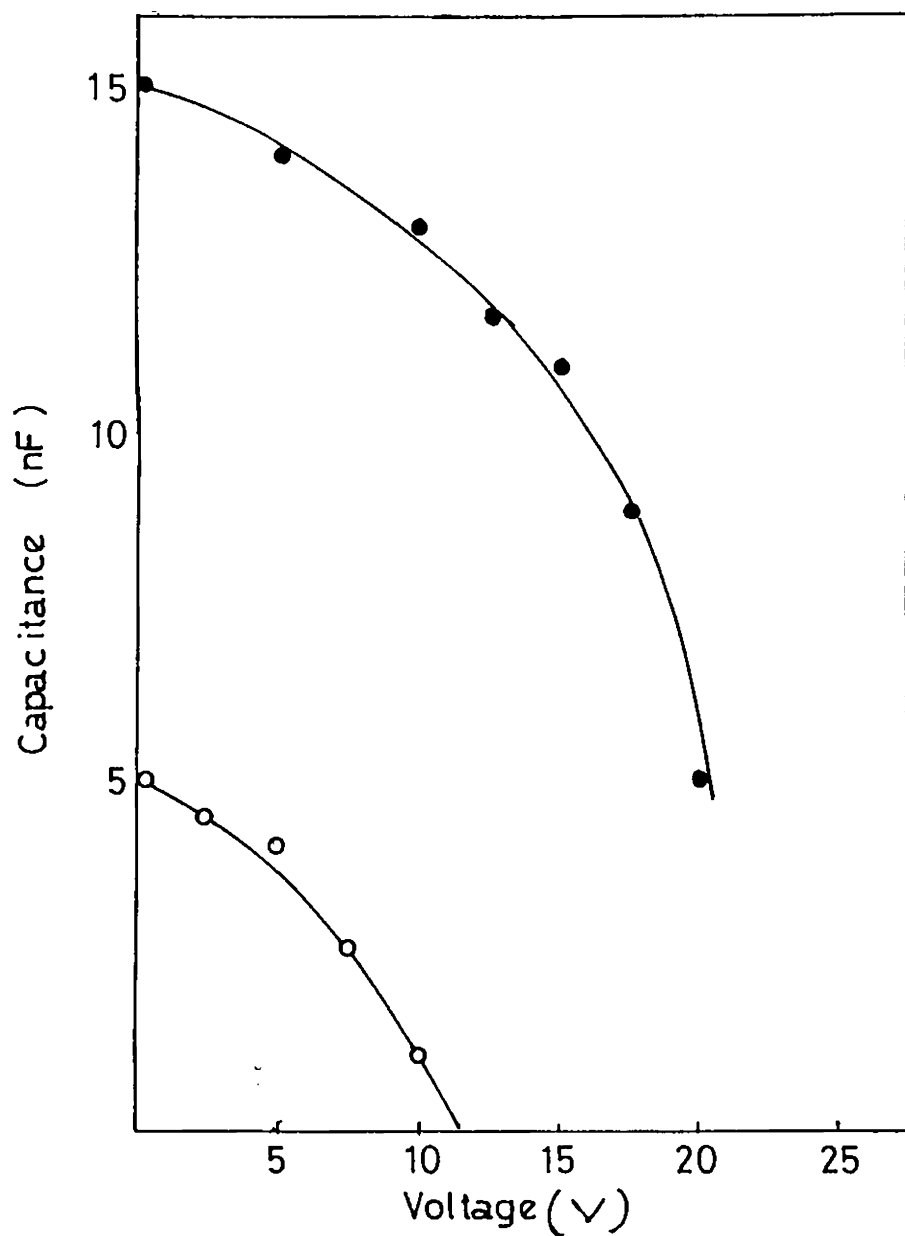two thickness—O—640Å, —●—510Å (AF films).

Fig.4.05  The variation of capacitance of the PAN films
with applied DC bias.  Film thickness —●—442Å
and —O—885Å for AF films.

an optical microscope of hundred times magnification. No
visible spots are observed. This supports that no conducting
filaments are formed by switching in this film.

4.14   Results and discussion

The dependence of threshold voltage on the film
thickness is investigated for the thickness range 500 to 1000Å.
It is found that the threshold voltage is weakly dependent on
the film thickness and is shown in Fig.4.06. There is compara-
tively large spread in the threshold voltage thickness plot.
The threshold voltage is found to be independent of the film
temperature for the range 300K to 400K.

The temperature coefficient of the film in the ON
state is found to be $1 \times 10^{-3} K^{-1}$ while these values for aluminium
and silver are   $4 \times 10^{-3} K^{-1}$. This indicates that the electrode
material is not migrating into the film. For conducting channel
formation the threshold voltage would show a temperature depend-
ence which is characteristic of thermoelectronic mechanism [10].
Moreover, the observation of switched film through an optical
microscope does not show dots, characteristic of filament
formation. Hence a conducting channel formation can be discarded.

The OFF state activation energy is found to be 0.66 ev
and for the ON state it is negligible as shown in Fig.4.07. For
a film that is not switched the activation energy is found to
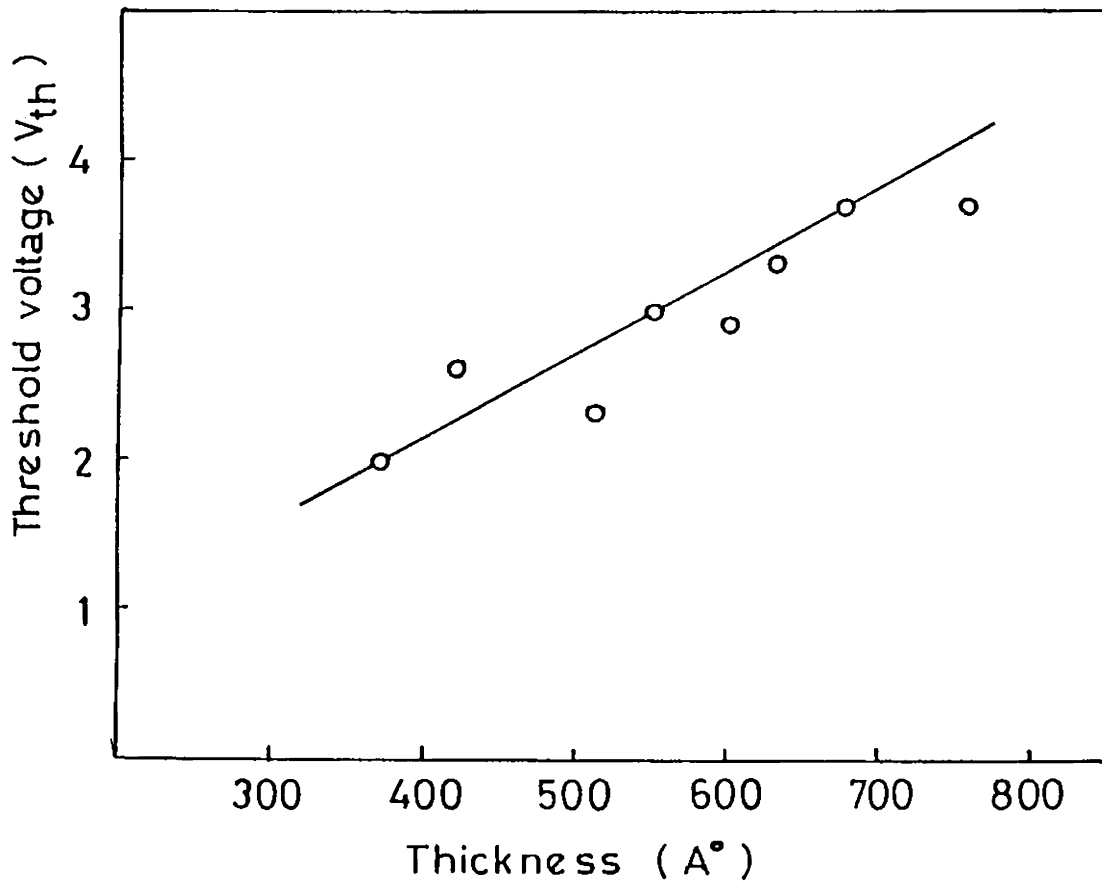
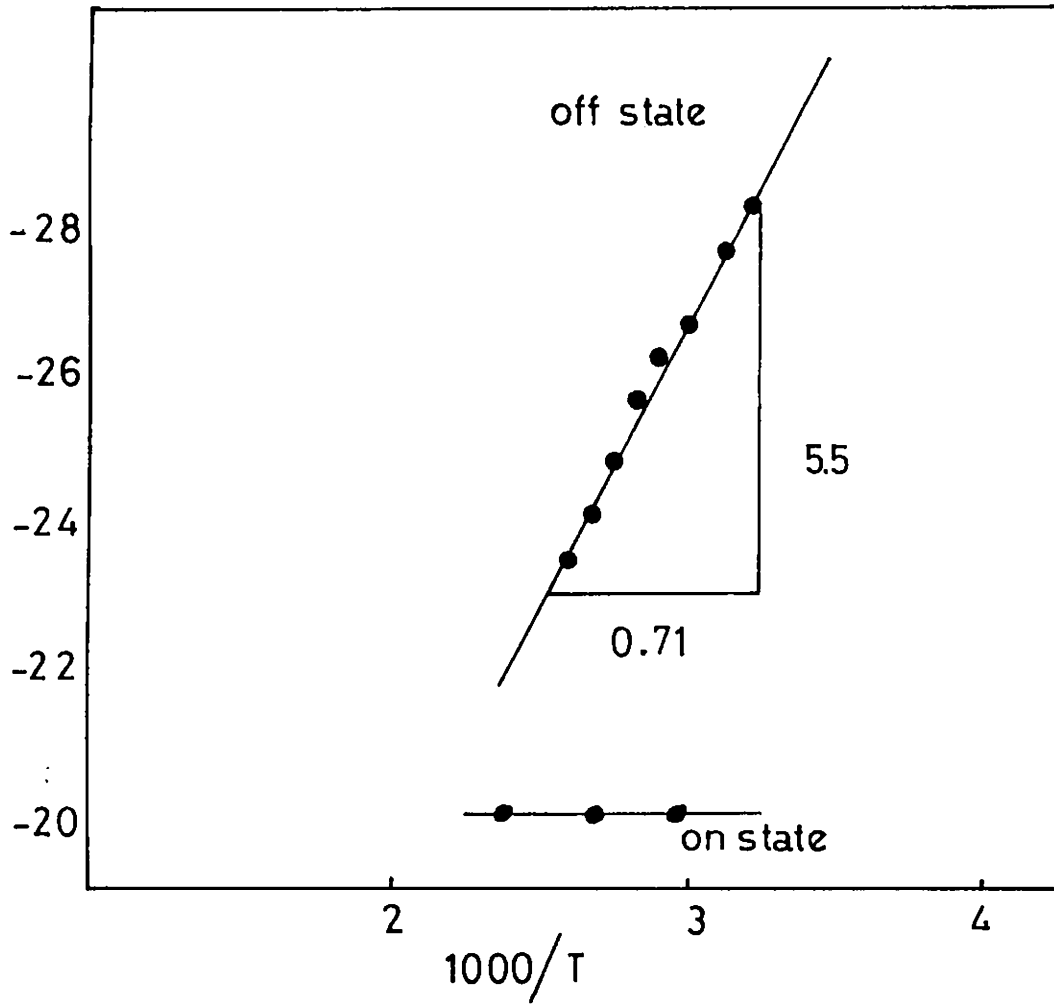Fig.4.06   Dependence of threshold voltage ($V_{th}$) on film thickness.

Fig.4.07 $\ell n.\sigma$ versus 1000/T plot for ON and OFF
states of AF-PAN films, film thickness 550Å
OFF state activation energy = 0.66 ev.

be 0.4 ev in agreement with the reported value [11] and is attributed to the orientation of dipoles. The higher activation energy of the electroformed films may be due to the change caused by charge migration [12].

The analysis of $\ell n I$ vs. $\ell n V$ characteristic shows four distinct regions Fig.4.08. For lower fields $(0.1 \times 10^6$ v/cm) the slope is 1/2. This is due to Poole-Frenkel conduction in this region with shallow traps. For fields in the region $0.1 \times 10^6$ to $0.28 \times 10^6$ v/cm an Ohmic region is found. For fields upto $0.54 \times 10^6$ v/cm the conduction mechanism is space charge limitted with a slope of 2.1 and finally the film showed a switched region.

These conduction regions are explained by the participation of traps, impurities and space charge formation. The plasma polymers are generally amorphous and are inherent with high acceptor and donor densities. Many amorphous films are shown to have switching behaviour [13, 14]. The donor impurity centres are shown to have remarkable switching contribution [15]. In amorphous materials the trap density is very high. From the threshold voltage $'V_{th}'$ and the thickness 'L' the trap density 'N' may be calculated [16] using the relation $N = \dfrac{\varepsilon \varepsilon_o \times V_{th}}{e \times L^2}$. Where $\varepsilon$ is the dielectric constant of the material and $\varepsilon_o$ the dielectric permittivity of free space and the calculated value
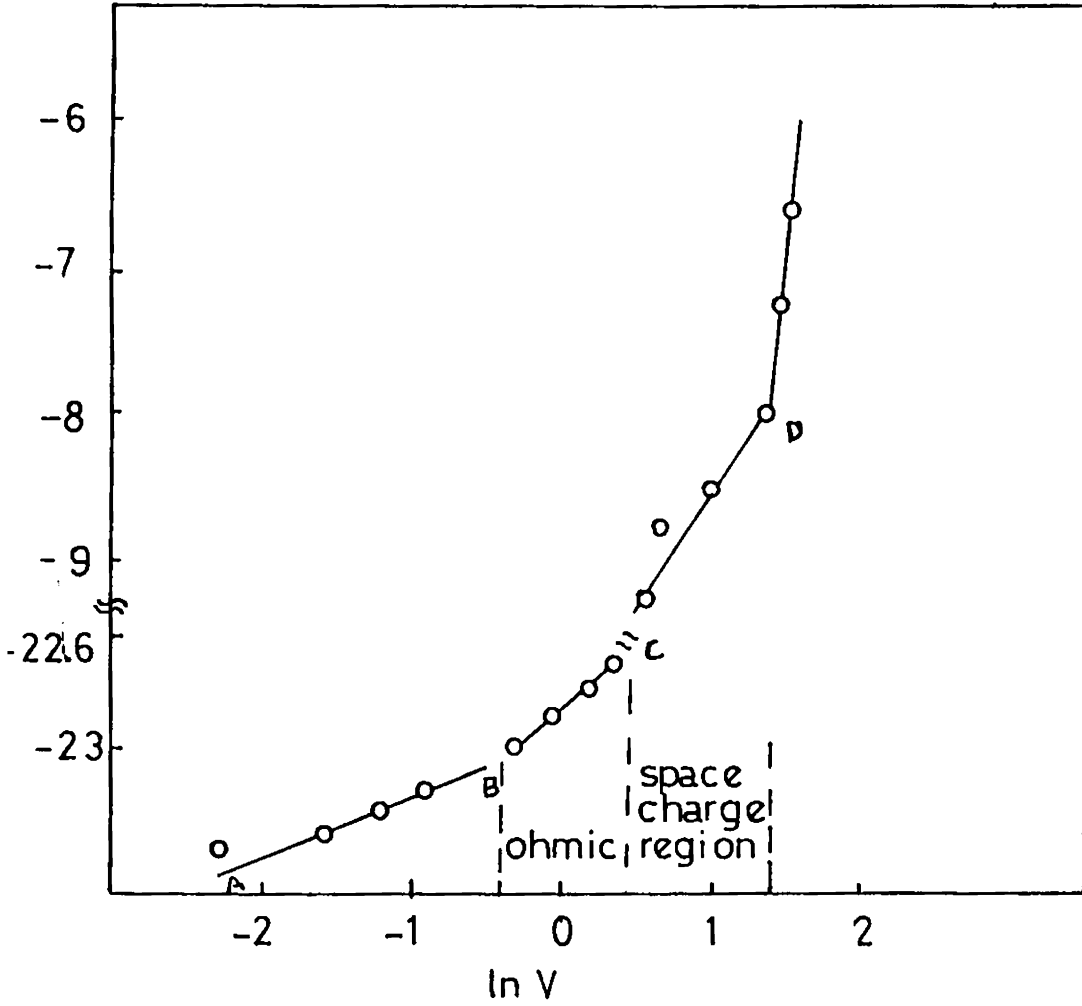
Fig.4.08  $\ell$n.I vs. $\ell$n.V characteristic for AF – PAN films, thickness 550A. The region A-B with slope ½ is due to Poole-Frenkel conduction, region B-C is due to ohmic conduction and the region C-D with slope $\backsim$ 2 is due to space charge effect.

is obtained as $1.095 \times 10^{12}/cm^3$. At high fields the traps and impurity centres get ionised. For the Poole-Frenkel region, shallow traps take part in the conduction mechanism. For higher fields deep traps and impurity centres get ionized across the forbidden gap of the material. These ionised regions together with injected charges cause a space charge region. The exact situation within the film is not clear. From the I-V characteristic the space charge region is evident in these films. It is this space charge formation that is responsible for the switching behaviour. Many properties like the variation of ON state resistance, capacitance variation with applied bias, temperature independent behaviour of switching and the weak dependence of threshold voltage on the film thickness, are successfully explained by this space charge formation. The memory state may be attributed to the high density of traps present in the amorphous polymers followed by their ionisation and charge storage capacity.

The observed increase of ON state resistance of the film can be explained in terms of recombination of charges. The charges stored in the polymer recombine to some extent. This raises the ON state resistance of the film. The recombination profile is exponential as expected. The film impedance usually rises from $\sim$300 Ohm to three or four Kilo Ohms. Eventhough the film impedance rose, the film is fairly conductive and is in the ON state.

The change of resistance of the film is also reflected in the capacitance of the film. The OFF state capacitance of the film is in the range of nano farads and the ON state capacitance is very low, as reported earlier [17] and is about a few pico farads. This shows that the film is more conductive rather than dielectric in nature. The inductive nature of the film is found to increase as the capacitance is decreased.

The temperature independent threshold voltage and the poor dependence of threshold voltage on film thickness are also explained by the space charge formation. The switching may be interpreted by the overlap of two space charges formed at the two electrodes, as explained in Chapter 1. The spreading of the space charge occurs throughout the film. In effect a conductive plasma is formed. This state of highly spread charges explains the temperature and thickness independent switching.

The switching OFF is effected only by the application of an voltage pulse with sufficient power. A steady voltage is not seen to switch off. This implies that the pulses cause an injection of charges leading to the neutralization of the ionised centres. Higher frequencies, larger pulse width, and voltages fairly higher than the switch on voltage are found to easily switch OFF the ON state. The higher frequency of pulses used to switch OFF the film is found to have a predominant

effect. This shows that if higher frequency is used, it is
effective in transferring injection and neutralization of the
ionised centres of differing energy levels in the bulk of the
film.

4.20  SWITCHING IN DIRECT CURRENT DISCHARGE PREPARED PAN FILMS

The properties of polymer films depend very much on
the preparation conditions and methods used. The switching
investigation on direct current 'DC' discharge is carried out
to see whether this method would provide a stable switching
property. The results are found to be different from polymer
films prepared by AF  discharge.

4.21  Preparation of DC discharge PAN films

The preparation of films by direct current discharge
is made using the system described in chapter 3. Instead of
audio frequency, a DC power is used for polymerisation. The
DC power supply is schematically shown in Fig.4.09.

The polymer films are obtained on precleaned electrode
coated substrates. The polymerisation is done at a constant
pressure of 0.6 torr and 0.1 milliamp/$cm^2$ current density.
The electrodes are coated to form silver polymer aluminium
sandwich configuration. When both the electrodes are aluminium,
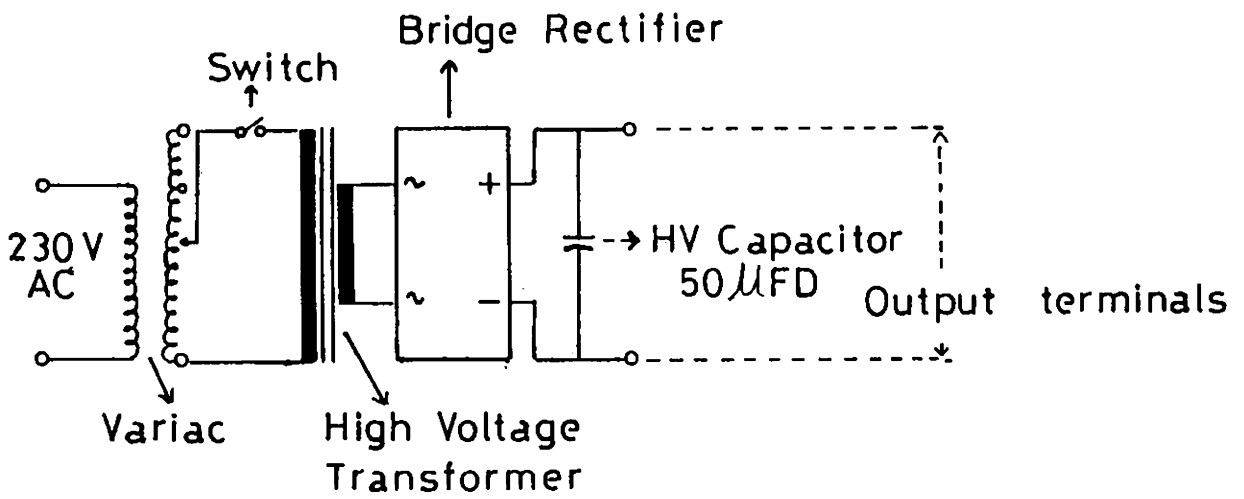the electroformation process is very difficult and  when both

Fig.4.09 Schematic figure of high voltage direct current
power supply.

electrodes are silver the stability of the film is found to be poor. So a combination of these two electrodes are used with one aluminium and the other silver. This sample is kept in a chamber evacuated to 0.01 torr. The current voltage charact- eristic is plotted by using an X-Y chart recorder. Different electrode assembly like tin oxide-mercury and aluminium--silver combinations are used.

## 4.22 Results of the Experiment

The DC polymerised polyacrylonitrile films showed bistable switching property. The specimen current rose suddenly at a threshold voltage $V_{th}$. A negative 'S' shaped conductive region and a holding voltage $V_H$ are found in the I-V charact- eristic as shown in Fig.4.10. After the switching, the current rose linearly. Three to four orders of resistance change was found in these films. When the ON state resistance was brought to a few hundred Ohms and left free it was observed that this ON state resistance increased exponentially to a few kilo ohms as in Fig.4.11. The OFF state was attained by applying a suitable pulse voltage. Large pulse width and higher frequency pulse were found to switch OFF the film easily. The ON-OFF commutation is possible for a large number of events. For a film having an OFF state resistance greater than twenty megohm and an ON state resistance of two hundred Ohm, no order change of capacitance was observed upto one mega hertz of frequency.
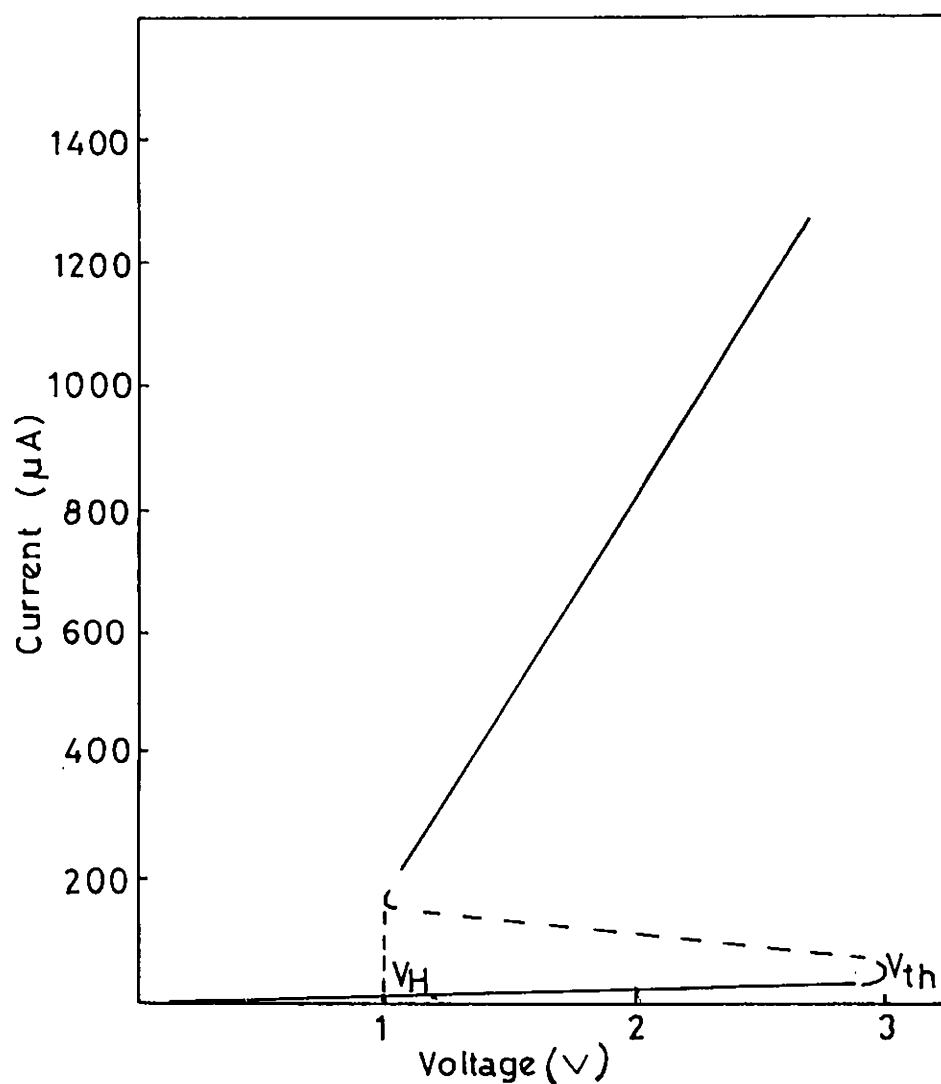
Fig.4.10   The current-voltage, switching characteristic
for direct current discharge prepared PAN films
thickness -743Å, $V_{th}$ - threshold voltage and
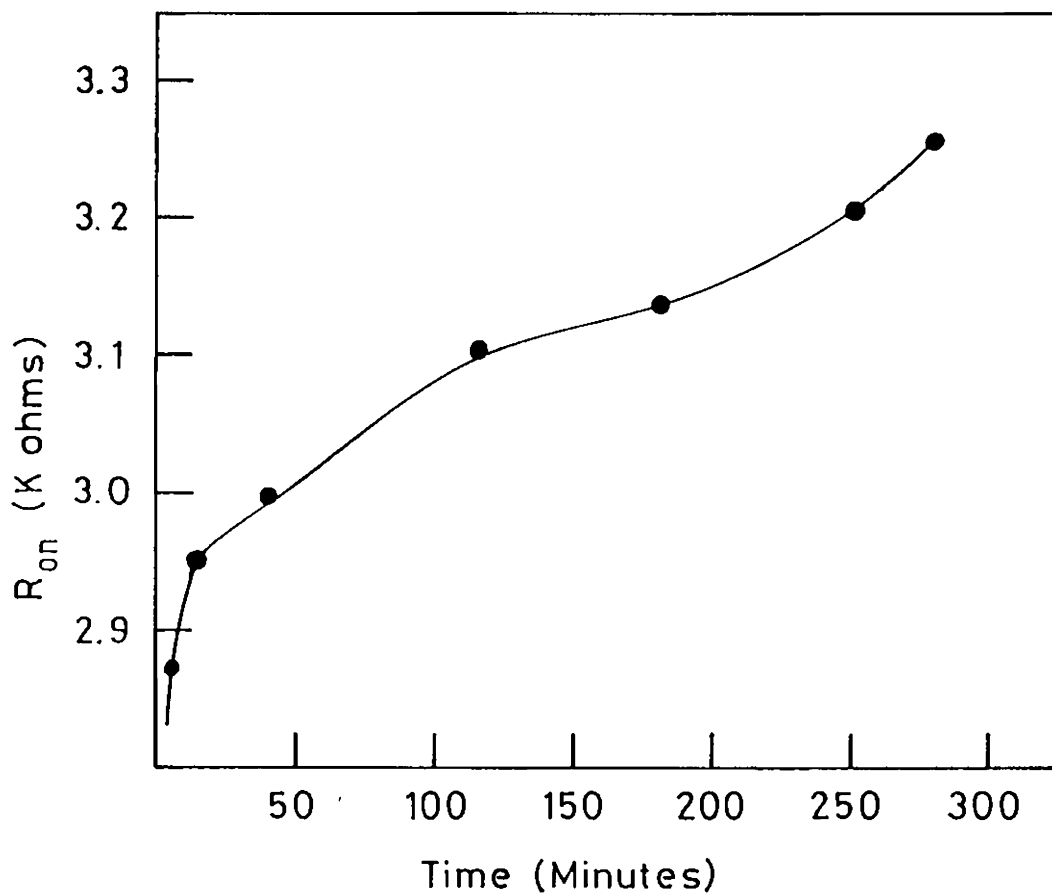$V_H$ - the holding voltage.

Fig.4.11   The variation of ON state resistance for
DC-PAN films, film thickness 826Å.

However, a dead short film which cannot be switched OFF showed negative capacitance. The negative capacitance is due to conducting channels [15]. The investigation of switching threshold voltage for the thickness range 500Å to 1000Å showed that the threshold voltage is independent of film thickness as in the case of AF films. Such a behaviour was reported by Simmons and Verderber, [18] and Szymanski et al.[19]. The effect of temperature on the switching threshold voltage in the range of 300K to 430K was also investigated. It was found to be independent of temperature. This was also observed in low temperature upto 148K.

In order to directly observe the film after switching, one electrode used was made of a conducting transparent tinoxide. The film on tin oxide was immersed in mercury and switched repeatedly as earlier. On examining through an optical microscope (x100) no change of morphology was noticed before and after switching. The temperature coefficient of resistance was found to be $0.006K^{-1}$. The ON state capacitance does not show a decrease on increasing the bias voltage but increased with frequency upto one mega hertz. Actually the frequency and the voltage of the bridge cause a resetting of the ON state resistance. Thus no change of capacitance may be observed eventhough a change is actually present. This may be the result of higher trap density present in DC films $(5.4x10^{16}/cm^3)$ which is four orders higher than AC films.

4.23 Discussion: Comparison of AF and DC polymer film
      switching properties

Switching in direct current discharge polyacrylonitrile
thin films are very similar to that observed in the case of
audio frequency prepared polyacrylonitrile films. The polymer
film obtained by this method is also amorphous and the trap
density is four orders more than the audio frequency prepared
polymer film. The switching is explained by the space charge
formation in the case of audio frequency prepared polyacrylo-
nitrile films. In the case of DC thin films the threshold
voltage is independent of both film temperature and film thick-
ness. This is explained by the presence of space charge formation.
The current voltage characteristic is different in the two cases.
In the case of AF film the switching profile is as in Fig.4.02
with a threshold voltage and sharp increase of current but
without an voltage drop from the threshold value. While in
the case of DC film an 'S' shaped characteristic as in Fig.4.11
is seen. An voltage drop is noticed with a holding voltage $V_H$.
This voltage drop may be due to the large density of ionised
traps and space charge formation. The ON state recombination
rate in DC film is about double the rate of recombination in
AF film. This also supports the higher density of recombination
centres which may be the trans or impurity centres. The same is
true in the case of variation of capacitance with the applied
voltage.

A three order capacitance change is found in the
case of audio frequency polymer films. But no capacitance
change is observed in the case of DC films. Actually there
would be a change of capacitance. But the lowest frequencies
(10 KHz) and voltage of the measuring bridge would be sufficient
to reset the ON state to high impedance state and is actually
observed. The capacitance is found to increase for both AF
and DC films with frequency. The temperature coefficient of
resistance is found to be $1x10^{-3}K^{-1}$ for AF films and $6x10^{-3}K^{-1}$
DC films. This shows that the resistance rise is higher for
DC films for a specific range of temperature. The dependence
of $V_{th}$ on the film thickness is poor in the case of audio
frequency prepared films while no such dependence is noticed
for direct current discharge films. However no difference in
order of switching field is noticed for DC and AF films. For
both films the switching states are stable for many months.
Eventhough there are good similarities of properties for both
audio frequency and direct current discharge films there are
some differences too and is attributed to changes in structure
[20] due to the differences in the methods of preparation.

# REFERENCES

1. R.J.Comstock, S.I.Stupp and S.H.Carr, J.Macromol.Sci.Phys. **B13(1)** (1977) 101.

2. J.Van Turnhout, Electrets, Topics in Appl.Phys.33, G.M.Sessler (ed.), Springer Verlag, New York, 1980, p.106.

3. J.A.Mayers, J.Non-Cryst.Solids, **79** (1986) 57.

4. K.Mohanachandran, Ph.D.Thesis, Deptt.Physics, Cochin University, 1983.

5. D.B.V.Parker, Polymer Chemistry, Applied Science Publishers Ltd., London, 1974, Ch.IX, p.119.

6. K.L.Chopra, S.Major and D.K.Pandya, Thin Solid Films, **102** (1983) 1.

7. J.L.Vossen, Phys.Thin Films, 9 (1977) 1.

8. G.Haacke, Annu.Rev.Mater.Sci. 7 (1978) 73.

9. H.S.Soni, S.D.Sathya and B.Sinha, Indian J.Pure and Appl. Phys. **21(4)** (1983) 197.

10. J.Swiatek, Thin Solid Films, 41 (1977) 5.

11. Y.Takashashi, J.Phys.Soc.Jpn. 16 (1961) 1024.

12. P.K.C.Pillai, J.Macromol.Sci.Phys. **B17(1)** (1980) 69.

13. C.Feldman and K.Moorjani, J.Non-Cryst.Solids, 2 (1970) 82.

14. A.K.Ray and C.A.Hogarth, Int.J.Electron. 57 (1984) 1.

15. M.A.Cohen, C.Morris, James D.Penar, J.Non-Cryst.Solids, 2 (1970) 91.

16. J.Swiatek, Thin Solid Films, 61 (1979) 321.

17. R.Vogel, Appl.Phys.Lett. 14 (1969) 216.

18. J.G.Simmons, R.R.Verderber, 301 (1967) 1386.

19. A.Szymanski, D.C.Larson and M.M.Labes, Appl.Phys.Lett. 14 (1969) 88.

20. Shinichi Takeda, J.Appl.Phys. 47 (1976) 5480.

# Chapter 5

## SWITCHING IN AMORPHOUS SILICON THIN FILMS

## Abstract

Amorphous silicon films are prepared by vacuum evaporation using tungsten filament heating and also by direct evaporation by an electron beam gun. The electrical switching investigations have been carried out in these amorphous silicon thin films. The effects of film thickness and film temperature on the switching threshold voltage have also been studied. The gun evaporated films are found to be superior to filament evaporated ones. Threshold switching is found to be prominent in these films.

155

## 5.00 INTRODUCTION

The investigations of switching in amorphous silicon thin films are taken up for a better understanding of the switching phenomena in the polymer films. There are a good number of inorganic materials especially oxides that are found to show switching behaviour. Now a days the importance of amorphous silicon films as devices has increased. Silicon films after passivation of the dangling bonds by hydrogenation are finding applications in several important fields such as electronics [1] and solar devices [2].

Switching in amorphous evaporated silicon films are first reported by Feldman and Moorjani [3]. Dey et al. [4] observed threshold switching in homogeneous films of evaporated amorphous silicon with titanium contacts. Followed by this Boer [5] also reported threshold switching in $n^+$-i-$n^+$ where i stands for intrinsic material. Owen et al. [6] studied high speed switching in $p^+$-n-i structures of a-Si films. They found forming process in their samples which is a charge controlled process. Owen et al. reported polar memory switching in glow discharge hydrogenated amorphous silicon [7]. Recently Shubhra Gangopadhyay reported reliable polar memory switching in sputtered a-Si:H with $p^+$-n-i structure [8]. Switching is also observed in junctions of silicon with

different materials. Polarity dependent memory switching
is observed in the case of a a-Si/$In_2O_3$-$SnO_2$ thin film
junctions [9] and memory switching is also observed in the
case of ZnTe-Si junctions [10].

In the present case we have investigated switching
in amorphous silicon films obtained by evaporation from a
tungsten basket source and also by electron beam gun evapora-
tion. In the case of films prepared from a tungsten basket
source, the threshold voltage is found to depend on the film
thickness of the material. The conductivity as well as the
threshold voltage show a change after certain thickness.
However this is not observed in the case of electron beam gun
evaporated films.

## 5.10 PREPARATION OF AMORPHOUS SILICON (a-Si) BY EVAPORATION USING THE TUNGSTEN BASKET

The preparation of amorphous silicon films for
switching investigations is carried out by evaporation from
a tungsten basket. The tungsten basket is prepared from
multistranded wires. The evaporation is carried out in a
separate system. This evaporation system consists of a six
inch diffusion pump backed by a 500 litres/minute rotary pump.
The evaporation is carried out at a vacuum of $10^{-5}$ torr.

Initially the tungsten basket is fired several minutes well above the melting point of silicon. This will minimise the impurities from the filament. Granules of polycrystalline silicon of purity 99.999% (Balzers) are placed in the basket and high current is passed through the basket. The silicon granules melt and wet the tungsten basket. The evaporation takes place slowly. The amorphous silicon films are obtained on the electrode coated substrate at the desired area of the electrode. The electrodes are made from aluminium by vacuum evaporation on to precleaned substrates. After the evaporation of amorphous silicon films, counter electrode of aluminium is evaporated so as to obtain one centimetre square area of aluminium-silicon-aluminium sandwich structure. The silicon films are brown in colour and have very good adhesion to the substrate and the aluminium electrode. This aluminium-silicon-aluminium sandwich structure is subjected to the switching investigation.

## 5.11  Switching in evaporated a-Si films

Fresh specimens of aluminium-silicon-aluminium sandwich structures are subjected to current-voltage characteristic investigation. This sample is kept in the metal electrical chamber with necessary electrical connections. The switching investigation is carried out using the experimental set up described in Chapter II. The aluminium

electrodes used form ohmic contacts to silicon at lower fields. The I-V characteristic is as shown in Fig.5.01. The current is found to shoot to milliamperes range after the threshold is attained. The dynamic resistance is lowered to the ohms region. The switching pattern and the threshold voltage are found to be the same for repeated cycles.

The switching investigation is carried out for the thickness range of $500\overset{o}{A}$ to $900\overset{o}{A}$. It is observed that the threshold voltage is found to depend on the film thickness (Fig.5.02). For thicknesses less than $600\overset{o}{A}$ the threshold is higher and the observed switching is threshold switching. In this type of switching, the impedance state is lowered to the conducting regime only for the period when the applied voltage is greater than the threshold voltage. For films of thicknesses greater than $600\overset{o}{A}$, the films showed a memory effect. A stable memory state with three or four kilo ohms resistance is observed. The conductivity measurements for the range of these thicknesses of evaporated amorphous silicon films showed a dependence of film thickness. This observation also supports the switching threshold voltage variation as in Fig.5.03. These independent measurements of threshold voltage and the film conductivity as a function of thickness are found to be in the expected order. The conductivity is very low for films
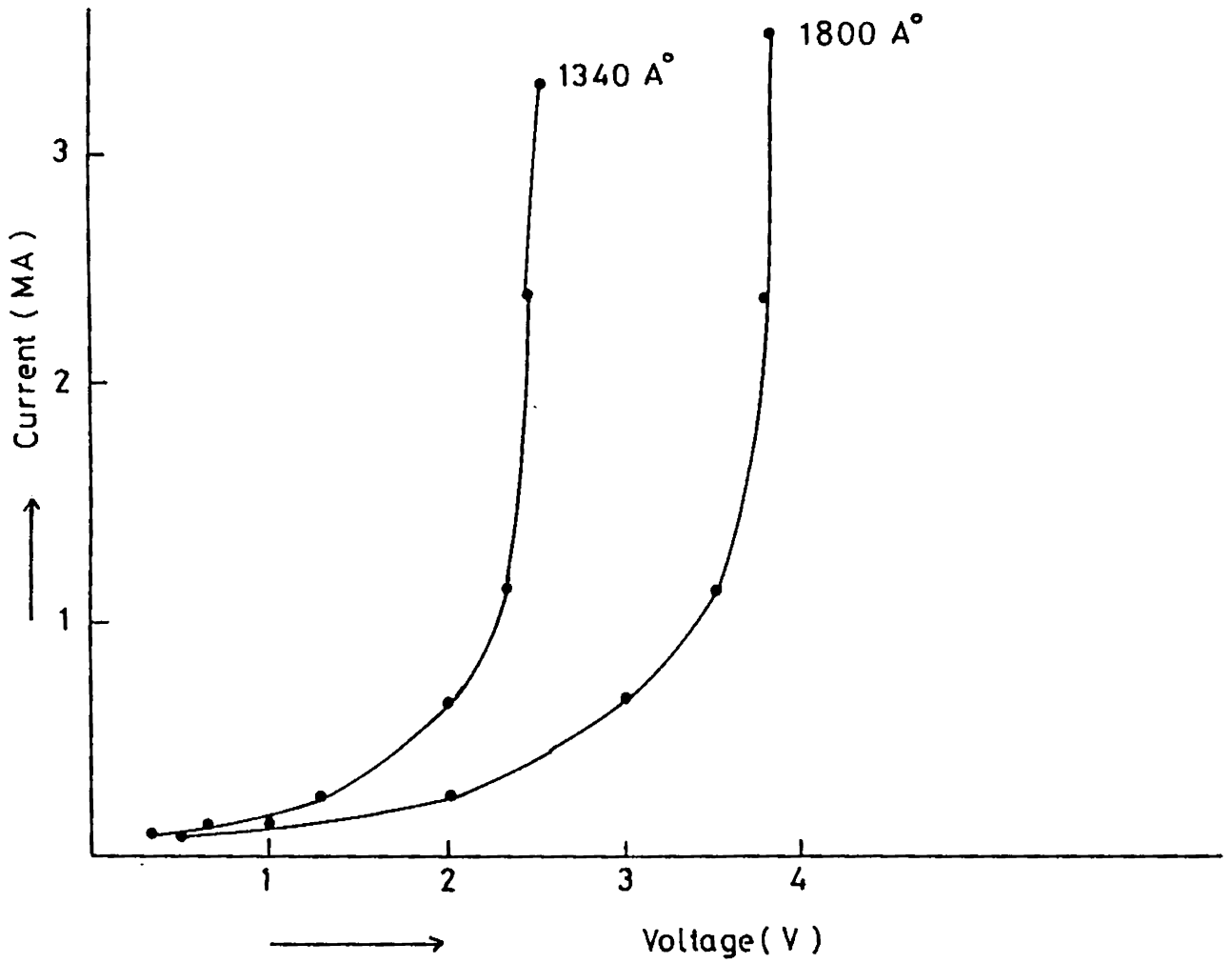
Fig.5.01  Current-voltage characteristic of filament evaporated
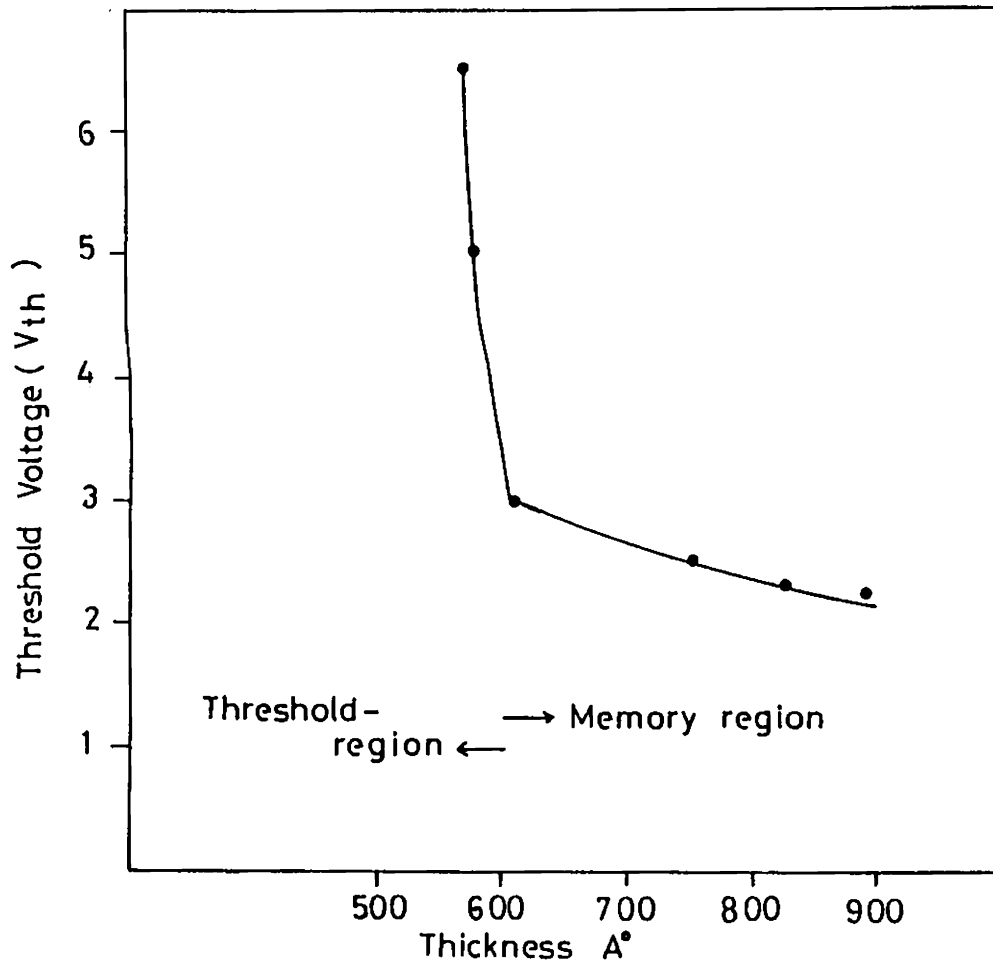a-Si films for two thicknesses.

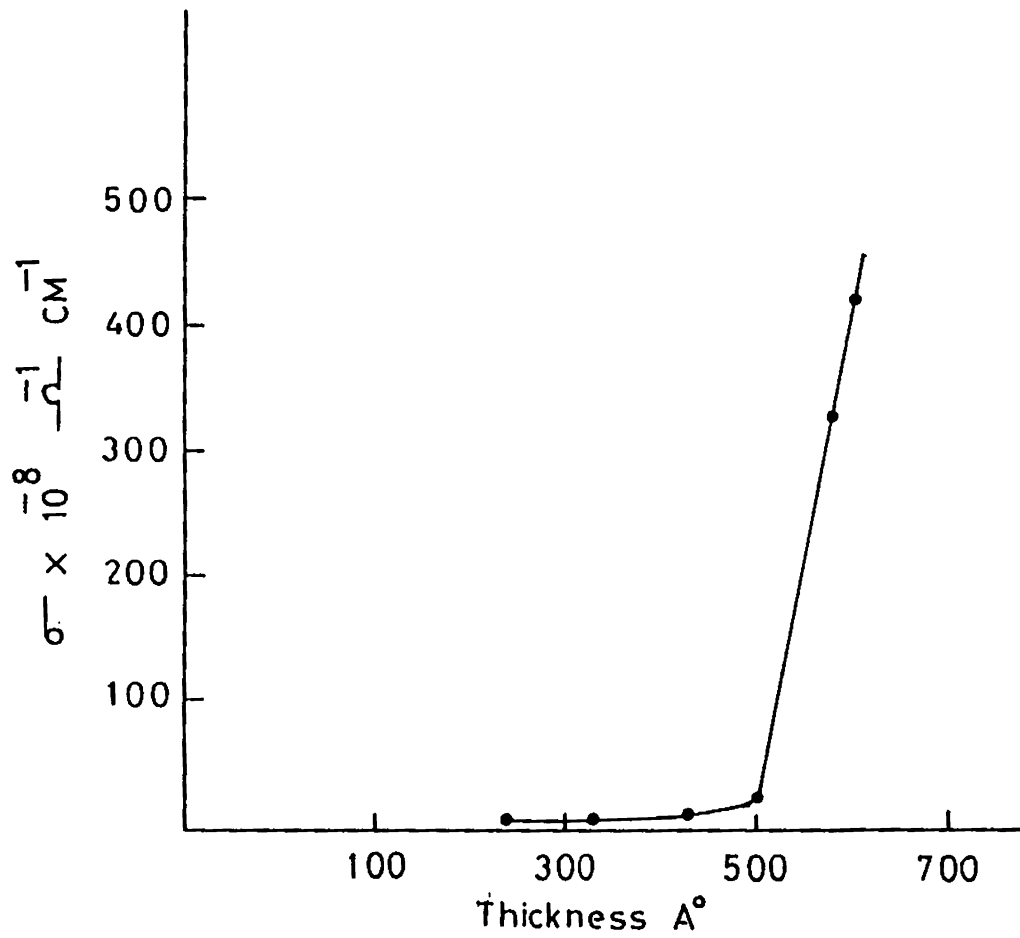Fig.5.02  Thickness versus threshold characteristic for
a-Si films.

Fig.5.03 Conductivity versus thickness for filament evaporated a-Si films.

of lower thicknesses ($<600$Å) and higher for thicker films.
The variation of film temperature on the threshold voltage
is investigated for the range of 300 to 383K. No change of
threshold voltage is observed in these samples for this range
of temperature. The films showed no change in the threshold
in air, oxygen atmosphere or vacuum.

From the $\ln I$ vs $V^{\frac{1}{2}}$ (Fig.5.04) plot, we see that
in the switching range the slope is greater than four. This
indicates that deep traps may be taking part in the switching.
The involvement of traps in the mechanism of switching is
evident. This is supported by the fact that the switching of
crystalline germanium is only effected after the irradiation
of the sample with $\gamma$-rays [11]. The effect of irradiation is
to break the bonds and form the traps. These traps act as the
switching centres. The ionisation of these traps causes the
switching while the neutralisation of these traps causes the
impedance to rise. The evaporated silicon is amorphous in
nature. These amorphous films are with very high defects and
the dangling bonds act as traps. Now the observation of
threshold voltage for thickness less than 600Å might possibly
due to the lesser density of traps. These traps are unable to
interact and overlap their wave functions as the thickness is
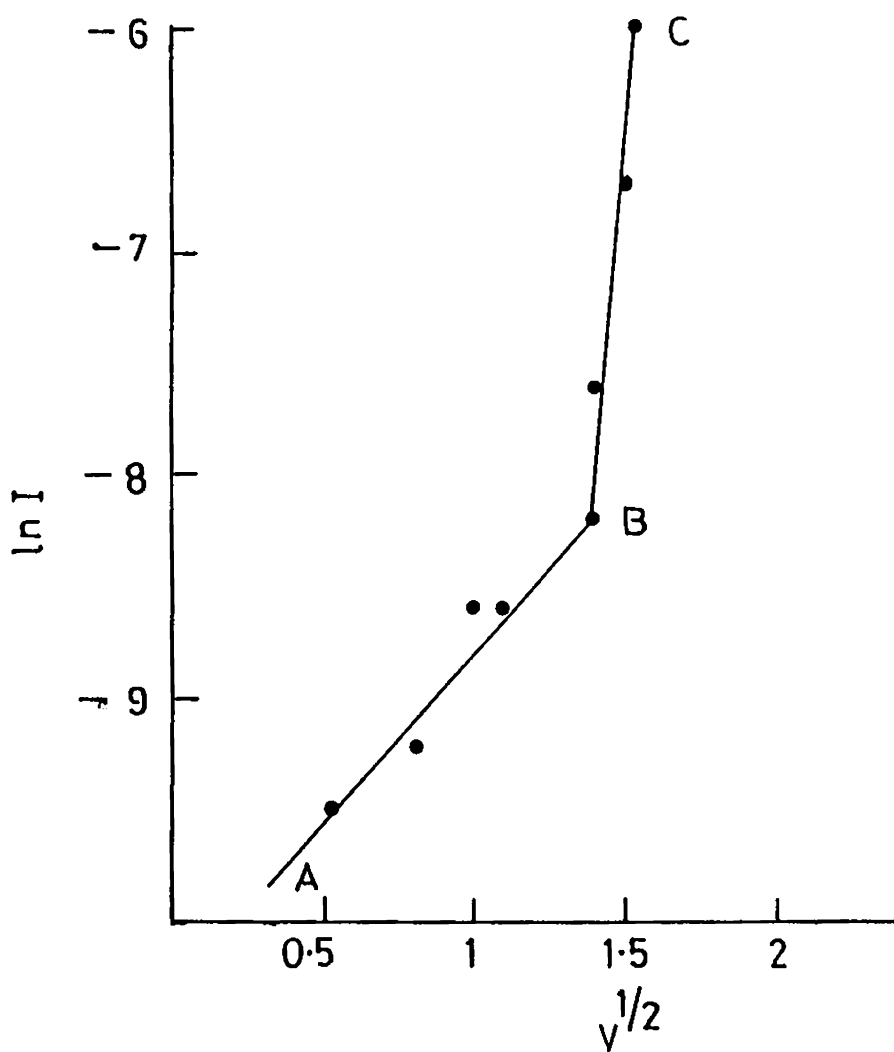small. Moreover, the substrate must have an influence over

Fig.5.04  $\ln I$ vs. $V^{\frac{1}{2}}$ characteristic of a-Si film.
Thickness 1800Å, in the switching range B-C
the slope is greater than four.

this thin film. The traps are neutralised easily. As the thickness of the sample is increased higher order of the film is attained, the traps behave in a co-ordinated way and their interaction becomes higher. The memory may be thought of as the result of higher trap density and charge storage ability. Actually an increase in the order of the film is reported [12] in the case of sputtered amorphous silicon as the film thickness is increased. There may be a critical threshold density of traps for memory switching.

## 5.20  ELECTRON BEAM EVAPORATION

The films prepared by electron beam evaporation are smoother than films prepared by conventional thermal evaporation. Electron beam deposition facilitates highly pure, stoichiometric thin films. Also materials with extremely high evaporation temperatures can easily be deposited by this technique.

In the present case a 3 kW electron beam evaporation unit supplied by M/s.Hind High Vacuum Company is fitted to a home made system. The electron bombardment heating arrangement consists of a heated tungsten filament source to supply electrons. These electrons are accelerated by applying a positive potential (ground) to the material and is focussed

to it by a magnetic field. The electrons lose their energy in the material very rapidly, their range being determined by their energy and the atomic number of the material. Thus the surface of the material becomes molten and evaporation takes place.

The present system has a bend beam (180°) water cooled pedestal with four crucibles for the evaporation of different materials by which sequential deposition on single substrate can be done in one vacuum cycle. A low tension transformer (10V, 30A) is used for the filament heating. The filament is kept at -6 kV which can be varied from -5 kV to -7 kV by adjusting a potentiometer. This facilitates a 2 mm shift in the striking point of the beam. The filament voltage and the beam current can be measured on the front panel meters and the power supply unit. The evaporation rate can be controlled by adjusting the beam current. With the remote control facility this can be done by visually monitoring the source. The current and voltage stabilisation in the circuit maintain the beam current and voltage constant irrespective of the line and load fluctuations.

5.21 Evaporation of silicon using electron beam gun

The evaporation of silicon is carried out by using the electron beam gun set up. Thoroughly cleaned glass

substrate after the coating of aluminium electrode is placed in the chamber. Proper masking is done so that silicon is evaporated to the desired area of the electrode. In order to facilitate easy evaporation the silicon pellets are placed in a graphite crucible. The graphite crucible has an inner diameter of 0.7 cm and an outer diameter of 0.8 cm. This crucible exactly fits into the copper crucible of the electron beam gun. The graphite crucible minimises the heat conduction to the copper block. The molten silicon is a very good conductor of heat. This conduction loss is minimised by the crucible. The chamber is initially pumped to $10^{-5}$ torr. Water is circulated through the copper block to keep it cool. The power is switched on for both low and high tension. The beam current is controlled by a remote control potentiometer. The specimen is heated by increasing the beam current. Initially there will be degassing of the graphite crucible. This is minimised by repeatedly increasing and decreasing the beam current. Finally the evaporation of silicon from the molten surface takes place without losing the vacuum. Silicon is now evaporated till the desired thickness of the film is obtained on the electrode. The film is taken out and the counter electrode of aluminium is evaporated to form one square centimetre of metal-silicon-metal sandwich structure. The switching is investigated in these samples as described earlier.

5.22   Results and discussion

The switching investigations on the electron beam
gun evaporated silicon films are carried out for a wide range
of thicknesses (600Å to 4000Å).  In all the cases the observed
switching is threshold in behaviour.  The current voltage
characteristic is retraceable.  No memory is observed for these
films.  The effect of film temperature on the threshold voltage
is studied for the range of 300 to 383K.  No dependence of film
temperature on switching threshold voltage is noticed.  It is
observed that the threshold voltage is weakly dependent on the
thickness of the film.

From the investigations it is found that the switch-
ing in this case is threshold switching.  The threshold switch-
ing is electronic in origin.  The gun evaporated films are
homogeneous with lesser trap density.  This is reflected in
the homogeneous nature of switching in all the range of thick-
nesses of the films.  But in the tungsten filament evaporated
samples, variation of threshold voltage and also the memory
behaviour are observed.  The electron beam gun evaporation
thus is a superior method for film preparation.  Moreover, the
purity of the film is preserved as the evaporation is instan-
taneous from the surface.  Thus the impurity effects are also
very less.  The trap density will be thus very low in these

films. The impact ionisation of the traps and the avalanche multiplication [13] may be the probable mechanisms of this threshold switching. The role of deep traps must be prominent in this case also. The exact cause is not evident from the present investigations. The memory switching reported in the $p^+$-n-i structure is thus the result of doping and introducing electronic levels in the amorphous structure. This may be the case in the sputtered hydrogenated amorphous silicon film memory switching [8] reported earlier.

# REFERENCES

1. D.E.Carlson, Amorphous Thin Film Devices, Polycrystalline and Amorphous Thin Film Devices, Lawrence L.Kazmerski (ed.), Academic Press, New York, 1980.

2. W.E.Spear and P.G.LeComber, Fundamental and Applied Work on Glow Discharge Material, Topics in Applied Physics, V.55, Physics of Hydrogenated Amorphous Silicon, Joannopoulos and G.Lucovsky (ed.), Springer Verlag, Berlin, 1984.

3. C.Feldman and K.Moorjani, J.Non-Cryst.Solids, 2 (1970) 82.

4. S.K.Dey and W.T.J.Fong, J.Vac.Sci. and Technol. 16 (1979) 82.

5. W.den Boer, Appl.Phys.Lett. 40 (1982) 812.

6. A.E.Owen, P.G.LeComber, G.Sarrabayrouse and W.E.Spear, IEEE Proc. (Part I, Solid State Electron Dev.), 129 (1982) 51.

7. A.E.Owen, P.G.LeComber, W.E.Spear and J.Hajito, J.Non-Cryst. Solids, 50&60 (1983) 1273.

8. Shubhara Gangopadhyay, Jurgen Geiger Berne Schroder, Herbert Rubel and Stefan Iselborn, Jpn.J.Appl.Phys. 24 (1985) 1363.

9. Lewin Crottoru and E.Grunbaum, Thin Solid Films, **67** (1980) L9.

10. N.G.Patel, J.Mater.Sci. **22** (1986) 2097.

11. T.Wada, Y.Fukuoka and T.Arizumi, J.Phys.Soc.(Jpn.), **25** (1968) 165.

12. Bernard Ranchoux, Didier Jousse, Jean-Claude Bruyere and Alain Deneuville, J.Non-Cryst.Solids, **59&60** (1983) 185.

13. Kurt E.Peterson, J.Appl.Phys. **47** (1976) 256.

# Chapter 6

## SUMMARY AND CONCLUSIONS

### Abstract

Summary and conclusions of the different investigations are presented. The importance of plasma polymerisation and the switching behaviour are briefly given. Investigations of switching in polyfuran, poly acrylonitrile and amorphous silicon thin films are summarised.

The present work is mainly on plasma polymerised thin films. The technique of plasma polymerisation is fast growing and is a standard method of thin film preparation. The so prepared films are pinhole free and is mechanically and chemically superior. This method allows preparation of inorganic and organic films using plasma discharge at different power levels. Many of the different methods are described in chapter 2. Plasma polymer films find a variety of applications in medicine, engineering, technology, industry and other day to day life. This method would allow preparation of new materials, with co-polymerisation and modification of polymer materials. The polymers would be a promising class of material for advanced applications, in semiconducting, insulating and super conducting devices. New inorganic polymers are being synthesised now a days. The polymers of yittrium, zirconium and other rare earth materials recently reported is a major advancement towards inorganic polymer materials.

The importance of switching phenomena is described in the first chapter. Switching investigations form part of more general basic study of electrical properties of materials. Both threshold and memory switching phenomena are important in electronic field. In living beings, both these mechanisms of passage and storage of information are found. In this context

the importance of polymer materials becomes obvious. The property of life is also due to the protein polymer the DNA. The switching investigations in a few polymer materials are carried out with the hope of obtaining a superior technological switch and also for understanding the basic phenomena behind the switching.

The switching in polyfuran thin films is carried out and presented in chapter 3. Furan is a five membered cyclic compound with an oxygen atom. The switching in this film has been established as due to the formation of conducting channels. Prior to the filament formation, Poole-Frenkel conduction is found to occur. This is a bulk phenomenon and arises from traps and impurity ionisation. The traps are mainly due to the amorphous nature of the plasma polymer films. The switching exhibited in polyfuran films is memory switching. A linear dependence of threshold voltage is found with thickness and the threshold field is found to be $2.12 \times 10^6$ V/cm. The threshold voltage is found to decrease with the temperature and is attributed to conducting filament formation. The temperature coefficient of resistance of the film is $5 \times 10^{-4}$ $k^{-1}$. The OFF state activation energy is 1.55 e.v and for the ON state it is negligible.

The investigations were carried out for the radio frequency plasma polymer films also. The growth rate of radio frequency plasma polymer is very high. A comparison of switching is given for both audio frequency and radio frequency prepared polyfuran films. In both cases the general behaviour of switching is the same and is due to the conducting filament formation. A decrease in threshold field is noticed in the case of radio frequency prepared films than the audio frequency prepared films. This may be due to decrease in the trap density. The differences observed in the switching may be due to the differences in the general structures in these audio and radio frequency prepared films.

The switching investigations in polyacrylonitrile revealed that this polymer is also having bistable switching property. The polymer films are prepared by the method of plasma polymerisation. Four orders of resistance change is observed between ON and OFF states. The two impedance states are by and large stable. A change of capacitance from nano to pico farads range is observed for the OFF and ON states. The threshold voltage is found to depend weakly on the film thickness and is independent of film temperature. The OFF state activation energy is obtained as 0.66 e.v and is

negligible for the ON state. From the analysis of current

voltage characteristic it is concluded that the switching

is as a result of the ionisation of the traps present in

the polymer. For higher fields, these ionised traps and

injected charge carriers facilitate the formation of space

charges in the film. The ionised state of the film is

preserved due to the charge storage capability of the polymer.

This is evident from the exponential rise of the ON state

resistance of the film to a few kilo ohms. The trap density

calculated from the switching threshold voltage for audio

frequency prepared films is obtained as $1.095 \times 10^{12}/cm^3$ and

in the case of direct current discharge films it is higher

and is $5.4 \times 10^{16}/cm^3$. As a general rule the trap density is

lower for higher frequency plasma prepared films. In both

cases the mechanism of switching is concluded to be same.

The higher trap density in direct current discharge films

is reflected in the recombination rate shown by the resistance

change and the independent nature of threshold voltage with

thickness and film temperature. The absence of filament

formation is evident from the direct observation of switched

film with transparent conducting electrodes. Moreover the

absence of negative capacitance in the ON state is an

evidence for the absence of filament formation. It is concluded

that the neutralisation of the ionised centres is the chief

mechanism for the switching 'OFF' in these films. This is accomplished by a proper charge injecting pulse. The participation of space charge and traps is very clear. The memory switching is the result of very high trap density and charge storage capacity of the polyacrylonitrile films. The switchings in a transistor and PAN film are having close similarity. In both cases, the charge density play the important role of switching. The charge storage ability of the material is related to the memory behaviour. With proper doping and appropriate configuration the switching property of this material could be made use of in devices and this aspect deserves more studies.

Switching phenomenon is investigated in both vacuum evaporated (by using Joule heat) and electron beam gun evaporated silicon thin films. In the first case of evaporated films, thickness dependent behaviour of threshold voltage is found. Above certain thickness (600Å) the films showed a lower threshold voltage and memory. Below this thickness the switching observed is threshold in nature This is due to the low density of traps present in the thinner films. The thicker films must have higher trap densities and are able to interact resulting in the overlap their wave functions. In the case of electron beam gun evaporated films

the observed switching is threshold in nature. The films are highly homogeneous and pure. This highly pure and homogeneous films are with lesser trap densities. The ionisation of these traps by impact and avalanche must be causing the threshold switching. The involvement of traps is very clear from the investigation of switching in crystalline germanium and $\gamma$-ray irradiated germanium. Only the $\gamma$-irradiated samples showed the switching in which traps are created by the irradiation.

Important conclusions on the properties of polymer thin films with special reference to switching have been drawn from the studies. By appropriately modifying the various parameters stable switching devices are possible from polymer thin films. More studies in this direction are required for device applications.