STUDIES OF TEMPERATURE DEPENDENCE OF DIELECTRIC BREAKDOWN FIELD IN MOLECULAR LANGMUIR FILMS

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CERTIFICATE

Certified that the thesis entitled "STUDIES OF TEMPERATURE DEPENDENCE OF DIELECTRIC BREAKDOWN FIELD IN MOLECULAR LANGMUIR FILMS" which is being submitted by Sri Devendra Kumar Agarwal in fulfilment for the award of Doctor of Philosophy in Physics of the University of Roorkee, is a record of his own work carried out by him under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other degree.

This is further to certify that he has worked for a period equivalent to 24 months full time research for preparing this thesis for Ph.D. Degree at the University.

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ABSTRACT

Electrical properties of dielectric thin films have been a subject of intensive theoretical and experimental investigations for the last many years as these properties reveal their practical applications as insulating layers.Technological interest produced a great increase inthe efforts devoted to this subject. Particularly, interesting is the study of the dielectric breakdown behaviour of thin films. In the present work, 'built-up' Langmuir films of metallic salts of fatty acids such as barium stearate etc. have been studied. These studies have been greatly enhanced because of their role in the theoretical development of the subject and a variety of some highly miniaturised solid state dielectric devices. Incidently, such 'built-up' films of barium stearate etc., have recently been proved promising from this point of view.

A number of mechanisms and many theories of dielectric breakdown have been proposed from time to time but they do not provide a wholly satisfactory explanation of the various observed breakdown phenomena. As is well known, the temperature dependence study of the dielectric breakdown field in thin films has played a fundamental role in the development of the subject theoretically. Much of the recent work on breakdown behaviour of thin films

relatedto the temperature dependence of the breakdown field has been reported, which is evidently important from device application point of view.

The sandwich structures of the type Al-film-Al were obtained using 'built-up' films of the metallic salts of some long chain fatty acids $[CH_3(CH_2)_{n-2}COOH]$ with different number of carbon atoms in the chain length as the insulating media between two thermally deposited aluminium electrodes. Insulating films were 'built-up' using a delicate but simple technique of Blodgett and Langmuir. The films obtained by this technique are found to be ideally suitable for the present studies because of their highly uniform thicknesses which are closely controllable in low ranges (to 25Å) and are accurately known. These films have the added advantages of high structural perfection, high dielectric strength, easier reproducibility and good thermal stability which, of course, was essential for the present temperature dependent studies. A great care is, however, needed at all stages during film deposition to minimise accidental vibrations and dust contamination for obtaining films free from gross defects. These films are crystalline in nature forming hexagonal crystals with the symmetry axis (optic axis) perpendicular to the plane of the film.

It is shown that when a film insulation is used between two thin metal electrodes, a high breakdown

strength is observed. Temperature dependent d.c. breakdown characteristics of the 'built-up' films of barium palmitate, margarate, stearate and behenate have been studied in the temperature range, from 320°K down to liquid nitrogen temperatures(77°K). The investigations have been carried out on films of both moderate thicknesses (20 layers) and on ultra thin films(1-10 layers). Mainly, two breakdown events, widely different from each other i.e. 'onset breakdown' shown by an abrupt rise in the current and 'destructive breakdown' accompanied by a large scale destruction have been distinguished. For variable temperature measurements, the samples were placed in a self designed and fabricated thermal probe which formed a part of the cryostatic arrangement designed and fabricated by the author. Below about 200°K, the 'onset' breakdown field was found to be independent of temperature due to the tunnel dominated electron injection process from the cathode. Above about 280°K,Schottky emission or thermionic emission was taking place and the breakdown field was found to decrease with increase in temperature. In between these two temperatures (i.e. between 200°K and 280°K) the breakdown field is found to decrease slowly with temperature as both the tunnel and Schottky effects play their role in this range. These results are qualitatively in favour of Forlani-Minnaja's field emission theory. Incidently, it is now almost generally accepted that the principal mechanism involved in the electronic breakdown

is the formation of an electron avalanche and the Forlani-Minnaja theory best explains many of the results obtained. Some additional evidence have also been given to show the non-thermal and electronic nature of the breakdown events in the present film system.

Another aspect of breakdown i.e. the 'maximum breakdown voltage' at which a large area of the capacitor gets destroyed through sparks is also studied in the present work. It is also important from the device application point of view as it determines the practically important 'ultimate dielectric strength' of the film. It is observed that the breakdown field at which the film largely destroyed, decreases with increasing temperatures. This destruction has been illustrated through transmission and reflection photomicrographs. The V-J characteristics in the non-destructive phase have also been obtained and given in the present work. Since the modern theories do not describe in detail, the actual mechanism of destruction, the results on destructive breakdown event are not interpreted theoretically. However, a qualitative explanation has been provided to differentiate between the 'maximum breakdown voltage' classified by Klein and Gafni and that studied here. 'Single-holes' and 'propagating' breakdowns of the type Klein et al had observed in their work are also not observed in the present temperature dependent studies as the films have high structural perfection and are always free from gross defects and weak spots.

The variation of the 'onset' breakdown field under alternating electrical stresses, which are also very important from the device application point of view, have been studied in 'built-up' films of barium palmitate, margarate, stearate and behenate. The investigations have been made as a function of temperature (in the range 77°K to 320°K) at a fixed frequency (30 KHz) for 4 and 20 layers thick films and as a function of frequency (in the range 10 KHz-100 KHz) at a fixed temperature (77°K) for 4 and 20 layers thick films. The temperature-breakdown field curves show a similar nature to that observed with d.c. voltages but the breakdown fields are found relatively smaller to the corresponding d.c. ones. These results could not be interpreted theoretically because of the lack of an adequate breakdown theory for a.c. fields. An increase in the breakdown field is observed with increasing frequency which contradicts the prediction of thermal breakdown theory, thus, showing the non-thermal nature of the breakdown events observed in the present film system.

All the data presented may be important from both theoretical and technological point of view as the potential devices may be required to operate at various temperatures.

The following is the subject matter of the thesis which has been arranged in eight chapters:

Chapter I- Various breakdown theories have been reviewed in this chapter and categorised in two principal theories i.e. 'electronic' and thermal breakdown theories'. The former which seems to be relevant in the present studies, has been discussed in detail.

Chapter II- This chapter reviews the experimental investigations by other workers on electrical properties of 'built-up' films, particularly, emphasis has been given to the temperature dependent studies of dielectric breakdown field in thin evaporated film systems. Previous studies of dielectric constant, dielectric loss and resistivity in 'built-up' films have also been given.

Chapter III- In this chapter discussion of the surface tension phenomena, formation of monolayer on water-air interface, mechanism of monomolecular spreading on water, non-occurrence of polymolecular film and some fundamental information about the individual molecules is made very explicitly.

Chapter IV- The 'building-up' process of depositing the films (particularly Y-type of film) has been discussed in detail. The nature of these 'built-up' films and their structure, as studied through X-ray and electron diffraction and the past and recent studies on thickness determination of these films have been described.

Chapter V- The experimental details of thermal evaporation of aluminium under vacuum, sandwich fabrication, selection and cleaning of the substrate and electrical set-up and measurement methods have been given in this chapter. Desirability and advantages of 'built-up' films which have stimulated interest in their studies have also been discussed.

Chapter VI- Discussion of the results of a detailed and systematic d.c. breakdown studies on 'built-up' films of barium palmitate, margarate, stearate and behenate have been made. Comparison of the results in terms of the known theories has also been reported.

Chapter VII- The results of a detailed and systematic a.c. breakdown studies as a function of temperature and frequency both in 'built-up' films of barium palmitate, margarate, stearate and behenate have been described. The interpretation of these studies is also given.

Chapter VIII- This chapter contains the summary of results on temperature dependence studies of breakdown field reported in earlier chapters and the importance of these studies. A possible future extension of the present work is also suggested.

Some graphs and representative photomicrographs concerning the results in Chapter VI and VII and various tables have been attached in the thesis.

CONTENTS

LIST OF FIGURE CAPTIONS

LIST OF TABLES

CHAPTER I

THEORIES OF DIELECTRIC BREAKDOWN

All the dielectric materials conduct electricity to a greater or lesser extent and suffer some form of breakdown when a high electrical stress is applied to these. The phenomena of dielectric breakdown in solids has been a subject of numerous investigations for a long time but still the basic mechanism of dielectric breakdown is a subject of great controversy and is little understood. The difficulties are of various origins. The theories of breakdown developed so far, do not explain the actual physical process of breakdown conduction but merely produce suggested criteria for the initiation of breakdown. Most of the experimental investigations in the dielectric films are, however, of recent origin but seem to make the phenomenon more clear. Experimental results are detailed enough to assess the evidence supporting theory and the observed facts. The principal physical variables over which the experimenter has a large range of control are the temperature and thickness of the insulating film used. The temperature range that has been covered commonly, is from liquid nitrogen temperatures upto about 100°C and the most satisfactory media in general was the inert liquids such as liquid nitrogen used for cooling the samples. Since the various theories in any case depend weakly or strongly on temperature and thickness, a knowledge of the effect of temperature and thickness on the breakdown strength can be of considerable importance in determining the breakdown mechanism.

One of the crucial points in the breakdown process is to establish whether the breakdown results from a strictly local chance event or rather is the consequence of a phenomenon propagating with an increase of intensity. However, the studies of breakdown field in thin dielectric films imply that the prime agent of breakdown is a phenomenon which propagates with an increase of intensity. One can presume that in solids the propagating phenomenon is an avalanche of charge carriers analogous to a better known mechanism of a discharge through a gas. This philosophy is not generally accepted because of the possibility of the breakdown attributed to a thermal effect as explained by some experimenters(1,2) i.e. the current density, even without an avalanche multiplication,generates more heat into the dielectric than the dielectric is able to dissipate. The breakdown phenomena in thin dielectric films, thus, seems to be based mainly on two principal theories i.e. electronic breakdown theories and thermal breakdown theories. Later, in the development of the subject, the electronic breakdown was subclassified into intrinsic and avalanche breakdowns. In the present chapter, all the three aspects of the breakdown theories have been described. The electronic breakdown theories have been discussed in detail as this mechanism seem to be dominant in the present case and the other one(i.e. thermal) in brief.

1.1 ELECTRONIC BREAKDOWN THEORIES

Probably the earliest approach to electronic breakdown was by analogy with the mechanical failure of the dielectric. In a manner similar to the attempts made to define the mechanical stability of the structure, Rogowski(3) attacked the problem of finding the electric field necessary to distort the structure sufficiently to loose its stability and termed it as 'electric tensile strength'. He proposed that this electric strength is a characteristic of the dielectric itself, being independent of other factors except its physical state and ascribe it to be electric, nonthermal breakdown to rupture an ionic insulator by electrostatic forces.

Although the mechanism of nonthermal breakdown in solids has been ascribed by many processes such as ionic processes, mechanical rupture, chemical decomposition of the substance etc., the most frequent interpretations are electronic. The principal theories of electronic breakdown in ionic crystals have concentrated mainly on the inception of breakdown leaving the actual destructive phase relatively **unexplored**.As has already been recognised some fifty years ago by Guntherschulze(4), the electronic breakdown phenomenon is due to electron ionization avalanches. This idea was first theoretically suggested by Rogowski(3) and developed by von Hippel(5) and Frohlich(6) while working separately on two different lines. Jofee and his collaborators(7,8) in their work also postulated an ionic conduction mechanism because of ionization. The experimental evidence of the electron ionization avalanche was given by Inge and Walther(9), Bozorth and Haworth(10), Shinohara(11) and von Hippel(12).

The older terminology of purely electrical breakdown includes theories of intrinsic and avalanche breakdowns. These theories have been current for some time possess some deficiencies but many times the combination of the two explains much of the results observed in various thin film systems. The problem of calculating the intrinsic breakdown filed have received the attention of von Hippel(13), Frohlich(6,14), Callen(15) and Frohlich and Paranjapee(16). The models proposed by these authors differ from each other by considering different mechanisms of energy transfer from the conduction electrons to the lattice and also by the different assumptions they make concerning the energy distribution of the conduction electrons. Several monographs and books have also been written by different authors. The references may be made to books and review articles of Whitehead(17), Frohlich and Simpson(18), Franz(19), Stratton(20) and O'Dwyer(21).

Two types of charge carriers, the ionic cores which are practically motionless and the loosely bound electrons, generally referred as conduction electrons should be considered for interpreting avalanche mechanism of breakdown in solids. But, while discussing about the insulators, as in the present work, the first and foremost question arises as to how these conduction electrons are originated, in this frame work, the occurrence of dielectric breakdown depends upon the presence of a large quantity of loosely bound electrons. Zeener(22) proposed for the first time the concept of internal emission causing electrons to jump from the valence band to the conduction band because of the applied electric field which was regarded as the origin of high density of the conduction electrons into the insulator, provoking the breakdown.

Another main line of development of avalanche breakdown theory has resulted from the realisation that space charges caused by the 'build-up' of an electron avalanche should result in a non-uniform field strength distribution. If one drops the assumption of a uniform field and treats the hole current as well as the electron current, then a natural basic theoretical assumption is continuity of current. There have been several attempts to formulate such a theory and all have a common feature in the sense they envisage breakdown as occuring when the space charge immediately in front of the cathode reaches such proportions that the electron current injected from the cathode is sufficient to destroy the material.

The intrinsic critical breakdown field is conceived as being the field strength for which some instability occurs in the electronic conduction current. The first such calculation of intrinsic critical field was given by Zeener(22), who calculated the rate of quantum mechanical tunneling from the valence band to the conduction band in the presence of a strong electric field. The zeener electric current is a strongly increasing function of the field strength and the instability criterion was chosen arbitrarily as the value of the field for which the current from the valence band exceeded some assigned value.

Intrinsic breakdown was also realised by von Hippel(23) as the bulk property of an infinite dielectric immersed in an uniform electric field. The original theories of von Hippel(24) and Frohlich(25) which were later reviewed by Franz(26), Stratton(20) and O'Dwyer(21,27,28) ascribe breakdown in insulators to electron avalanches produced by impact ionization. According to von Hippel(12) the electrons move in the field direction and gain energy proportional to the field strength by direct acceleration and the energy gain must exceed the loss (because of the electron-phonon scattering or due to the optical lattice vibrations) for electrons of all energy. This mechanism is generally known as 'low energy criterion'. The theory of von Hippel was expressed on the basis of quantum mechanical concepts by Seeger and Teller(29). On the other hand Frohlich(6) in his original theory of electronic breakdown in ionic crystals, assumed that at a sufficiently high field there occurs a rise in electron current due to impact ionization from the valence to the conduction band. Callen (15) elaborating on a suggestion of von Hippel(30) also devised a theory of electronic breakdown in ionic crystals. He used Frohlich's (6,25) basic approach but assumed that electrons with average energy must be able to accelerate to ionization energies before breakdown can occur. The fundamental ideas of Frohlich and Callen are same and both the theories predict an increase in breakdown strength as temperature increases.

Frohlich(6) lateron proposed another theory of electronic breakdown essentially based on avalanche mechanism as recognised by Guntherschulze(4) but different than that of the von Hipple's theory(12). According to him the electrons do not necessarily move in the direction of the field and are gradually accelerated. He instead assumed that the electrons change very frequently the direction of their motion just because of phonons and the net increase of their energy is proportional to the square of the field, as in the case of conductivity. Taking into account the electron scattering and assuming the rate of change of electronic energy on the average over many collisions to be positive (for at least some of the electrons) he led to consider the situation in which a group of fast electrons having a given mean energy would tend to have a net gain or loss of energy in their motion. The breakdown will ensue when this net energy gain of the electrons, in any case, exceed the loss for some energies including some smaller than the ionization energy of the dielectric crystal. This criterion is generally known as 'high energy criterion' of Frohlich. According to Frohlich's mechanism, the breakdown should occur when the applied field satisfies twc conditions: the field strength is such that the electrons are accelerated upto the ionization energy of the material and the breakdown field is the highest one for which a balance between the ionization collisions and the charge recombination is reached. The fact, that fluctuations occur in the energy of each electron and that the conduction electron energy distribution extends upto the ionization energy had also been introduced by Frohlich in respect of von Hippel's theory. Later, as summarized by O'Dwyer(31), Frohlich's breakdown field is found to be related to the temperature through the relation

$$F \; \alpha \left[1 + \frac{2}{e^{A/T} - 1}\right]^{1/2} \qquad \ldots (1)$$

where A is a constant peculiar to the dielectric and T is the absolute ambient temperature. However, it is remarkable to note that both the 'low energy' and 'high energy' criterion consider the dielectric to be essentially infinite in thickness and hence, predict no thickness dependence.

Presence of traps in the insulator may also have marked effect on the emission current. The theory of Penley(32) accounting these empty trapping centers was later elaborated by Gadzuk(33,34). According to band structure of solids an insulator is characterised by a full valence band separated from an empty conduction band by a forbidden energy gap of a few electron volts. Evidently, conduction can not take place in either the filled or the empty band unless additional carriers are introduced. If traps are present (as is the case with the amorphous substances), trapping of charge carriers can be expected to have a profound effect on the conduction processes. In the presence of traps, the conduction can take place by tunneling via traps. A model providing a number of isolated traps located within the energy span ΔV immediately below the conduction band of the dielectric was presented by O'Dwyer(35) which was originally proposed by Frohlich. According to this model, the process of transferring energy from the field to the lattice is by phonon emission resulting from electron transitions within the 'band', ΔV of trap levels. The result of this theory is given by

$$V \alpha e^{\Delta V/2kT} \qquad \ldots (2)$$

where T is the ambient temperature, k is the Boltzmann's constant and V is the breakdown voltage. However, this theory is only applicable to the amorphous substances. and not to the crystalline insulators.

The actual process in the avalanche mechanism for the breakdown to occur is, that electrons possessing an energy slightly below the ionization potential gain energy from the applied field and liberate further electrons. This process requires a certain amount of time which decreases with the increase of the field strength. Obviously, in relatively thicker dielectrics most of the fast electrons spend a time in the dielectric greater than the minimum necessary to gain the requisite, then the electric strength remain uneffected because the period of acceleration merely distributes to the time lag of breakdown. On the other hand, if the dielectric is very thin, it may be necessary to increase the field strength beyond the value for thick specimens in order that the electrons may be more rapidly accelerated and gain an energy greater than ionization potential before they are lost to the electrodes. However, Frohlich(36) has studied precisely the energy distribution among electrons in a dielectric and he(37) had also indicated the order of the effect of thickness which does not involve this distribution.

A theory in which avalanche of electrons arises by field emission from the valence to the conduction band was considered by Zeener(22) and is known as field-emission breakdown theory. This theory attributes breakdown to an uncontrolled emission of electrons from the valence band of the dielectric to the conduction band. The theory is summarized by O'Dwyer(38) who gives a relation for the linearly increasing fields

$$F = \left[\frac{\beta}{\log\left[\frac{e\alpha\mu F^{22/3} N_v t_c^2}{\beta^2 C_v (T_m - T)}\right]} \right] \quad \ldots (3)$$

where α and β are two constants peculiar to the dielectric, μ is the electron mobility, t_c is the time of application of the field, N_v is the density of valence electrons, T_m is the temperature of the centre of the dielectric and T is the ambient temperature, C_v is the specific heat per unit volume and e is the electronic charge. This equation on solving by successive approximations shows a positive slope in the curves plotted between field and temperature. A theory of quantum mechanical field emission from isolated imperfections in a dielectric was proposed by Franz (19,26). His final result is given by

$$F \propto \frac{1}{\log\left[\frac{x_o}{\omega}\right]} \quad \ldots (4)$$

where x_o is the recombination length and ω is the thickness of the dielectric. This relation, however, does not seem to give a more realistic explanation of the functional dependence of the breakdown field.

In attempting to clarify the mechanism of current multiplication and destruction of the dielectric, Seitz (41) proposed another theory, commonly known as '40 generations theory'. He considers the conditions in which a single electron (or very few electrons) starting at the cathode in its travel towards anode can cause an avalanche of electrons of sufficient size to destroy the dielectric. If a single electron leaving the cathode can succeed in producing another conduction electron by ionization collision and these two produce further two, an avalanche of n electrons will be produced in n generations. Seitz, in order to estimate the avalanche size assumed that for the dielectric to melt, the avalanche must contain about 10^{12} electrons i.e. the initiating electron takes part in forty ionizing interactions during its travel, independently of the film thickness. If ω is the inter-electrode distance and α_0 is the reciprocal of the mean ionization length, the product $\alpha_0\omega \simeq 40$. If each electron of the avalanche reaches an energy E_1 sufficient to ionize, the ionization rate increases by increasing the electron energy. The probability P for each electron to get this minimum energy 'E_1' without suffering any phonon scattering is given by

$$P = \exp\left[-\int_{E_{av}}^{E_1} \frac{1}{\tau}\left(\frac{dE}{dt}\right)^{-1} dE \right] \qquad \ldots (5)$$

where E is the average electron energy, τ is the mean time between two interactions and dE/dt is the change in energy per unit time when the electrons do not interchange energy with the lattice. Therefore,

$$\frac{dE}{dt} \alpha F$$

where F is the applied strength. Seitz has made the assumption that τ is independent of E, then

$$P \ \alpha \ \exp(-H/F) \qquad \ldots (6)$$

where H is a proper constant. A simple justification for the form of equation (2) is given by Shockley(42). According to him, the probability $P(\ell)$ that a conduction electron has suffered no collision with the lattice over a length ℓ is given by

$$P(\ell) = \exp(-I/eF\langle\lambda\rangle) \qquad \ldots (7)$$

where I is the ionization energy and $\langle\lambda\rangle$ is the average value of mean free path for the electrons. If one assumes that all the field dependence of the ionization is contained in eq.(7) then a comparison with eq.(6) yields

$$H = \frac{I}{e\langle\lambda\rangle} \qquad \ldots (8)$$

and hence,

$$\frac{H}{F} = \log(\frac{\alpha\ \omega}{40}) \qquad \ldots (9)$$

in which α is a quantity having the dimensions of inverse length.

A more exact discussion of this problem was given by Baraff(43) who solve the approximate Boltzman equation numerically for the case of constant mean free path and quasi free electrons. The results of these computations show that the pre-exponential term depends on the field strength in a non-negligible way unless the optical phonon energy exceeds about three percent of the ionization energy. This condition is almost not applicable in the case of insulators, so that eq.(8) must be regarded as rough approximation indeed. Due to the proportional dependence of α on P, 40 generation theory shows that reciprocal of the breakdown field varies as the logarithm of the dielectric thickness (eq.9). Since H will presumably have a similar temperature dependence to that of the intrinsic breakdown fields, the forty generations breakdown field will be likewise temperature dependent. However, this theory is based upon the assumptions which are not easily acceptable. The first being that the electron energy just equivalent to the ionization energy is sufficient to start the avalanche and the second is that τ is independent of the electron energy.

Recently, Forlani and Minnaja(40,44) have proposed a theory of dielectric breakdown in solids based on the electron ionization avalanche mechanism taking into account the above two assumptions of Seitz. The physical hypotheses of this theory are that the dielectric is an ionic crystal and that the electrons in the conduction band are free. Two facts have been considered to reach the high electron density necessary for having breakdown. The first fact is an electron density in the conduction band dependent upon the applied field in a monotonic way and the second is a multiplication of this density because of an avalanche phenomenon. The avalanche process includes tunnel emission of electrons at the cathode into the conduction band of the dielectric and leads to a field dependent current density which reaches a value sufficient to produce breakdown.

Simmon's(45) equation for the injected current density for electrons injected into conduction levels from the cathode due to tunnel effect has been employed by Forlani and Minnaja (henceforth, referred as F-M) in conjunction with other hypothesis of avalanche mechanism (46) and following Fowler-Nordheim result(44,47). The resulting current density at the injected interface can be written as-

$$J_i = J_o \exp\left[- \frac{4(2m)^{1/2} \phi_{eff}^{3/2}}{3\hbar\ q\ F} \right] \qquad \ldots (10)$$

where q, m and $\hbar$ (=h/2π) are the electronic charge, mass of the electron and Plank's constant respectively, $\phi_{eff}(=\phi_\omega - \psi)$ is the effective height of the potential barrier at the cathode-dielectric interface [ϕ_ω is the work function of the cathode metal and ψ is the electron affinity of the dielectric to the metal], F is the applied field and J_o is the field dependent pre-exponent quantity which is given by

$$J_o = \frac{q(qF)^2}{16\pi^2 \hbar \phi_{eff}} \qquad \ldots (11)$$

The current density versus distance x from the injecting interface is obviously given by

$$J(x) = J_i \; P \exp\left[\frac{qF}{\bar{E}} \left(\frac{1}{x} + \frac{1}{x_o} \right)^{-1} \right] \qquad \ldots (12)$$

where $\bar{E}$ is the difference between the mean energy of an electron when it is able to ionize and the mean energy of the electrons emerging from an ionization event, x_o is the recombination length and P is the probability for the electrons to reach the unstable equilibrium energy (E_u) from the stable one (E_s). Equation (12) implies that the probability for an electron with the unstable energy to ionize is practically unit.

Obviously, this equation (12) attains its maximum value at $x = \omega$ where ω is the separation of the two metal electrodes. For $\omega \gg x_o$, the maximum current density is independent of dielectric thickness. Introducing the value of J_i from equation (10) into equation (12), the breakdown condition for $\omega \ll x_o$ can be written as

$$\frac{q\,F_B\omega}{\bar{E}} - \frac{4(2m)^{1/2}\,\phi_{\rm eff}^{3/2}}{3\hbar q F_B} + \log P + \log\left[\frac{q}{16\pi^2\hbar}\,\frac{(qF_B)^2}{\phi_{\rm eff}}\right] = \log J_B \qquad \ldots (13)$$

where J_B is a threshold current density above which melting or evaporation of the dielectric material occurs and F_B is the breakdown field of the dielectric.

When the field strength is larger, the most important term is the second one, at least for high frequency gap dielectrics. In this field range P and E are insensitive to the field strength and the fourth term on the left side and the term on right hand side are negligible in each case. Thus equation (13) turns out to be

$$F_B \simeq \left[\frac{4(2m)^{1/2}\phi_{\rm eff}^{3/2}\,\bar{E}}{3\hbar\, q^2}\right]^{1/2} \left(\frac{1}{\omega}\right)^{1/2} \qquad \ldots (14)$$

It is remarkable to note that the dependence $\left[F_B \; \alpha \; (\frac{1}{\omega})^{1/2}\right]$ is applicable for only high energy gap dielectrics and for not very large electron affinity. The electron injection at the negative electrode being the most important mechanism in thin dielectric breakdown, the third term (log P) in the left side could be predominant only for very large electron affinity. Considering this fact, the thickness dependence of the breakdown field strength should be proportional to $\omega^{-1/4}$, at least for the approximation assumed that the electron do not interchange with the lattice between two next effective collisions. It was also shown that this type of dependence holds if the effective height of the potential barrier is very low. This enables one to conclude that also for fields larger than high thickness breakdown field, for thin films, the injection electrons due to the tunneling travel along the bottom of the conduction band. Obviously, the behaviour expressed by equation (14) is independent of the temperature because of the basic mechanism implied i.e. the tunnel injection.

Experimental results consistent with equation (14) have been found for various inorganic dielectrics by Budenstein and Hayes(48), Smith and Budenstein(49) and Budenstein, Hayes, Smith and Smith(50). Recently reported, thickness dependence data of Agarwal and Srivastava(51,52) on the organic dielectric films (also chosen for the present temperature dependent investigations) show results perfectly in favour of the F-M theory.

The argument that sometimes the electron injection is governed by Schottky emission (44,53) rather than the tunnel effect, changes the whole picture and brings about an expression showing $F_B \alpha \frac{1}{\omega}$ which shows thickness independent nature of breakdown voltage, maintaining its validity, even if the voltage drops in a nonlinear way through the dielectric layer. In particular a transition from tunneling to Schottky effect could be expected when the applied field is very large due to the predominant role of electron image force on the shape of the potential barrier. In this case equation (10) must be replaced by the equation

$$J_i = A \exp\left[- \frac{\phi_{eff}}{(kT)}\right] \exp\left[\left\{ \frac{q^3}{4\pi\varepsilon\varepsilon_0}\right\}^{1/2} / (kT).F^{1/2}\right] \quad \ldots (15)$$

where A is the Richardson's constant, ε_0 is the free space permittivity and ε is the dielectric constant of the material under consideration and k is the Boltzmann's constant. Introducing this value of J_i (eq.15), equation(12) becomes

$$\frac{q\ F_B \omega}{\bar{E}} - \frac{\phi_{eff}}{kT} + \frac{\left[q^3/(4\pi\varepsilon\varepsilon_0)\right]^{1/2}}{kT} F_B^{1/2} + \log P + \log A = \log J_B \quad \ldots (16)$$

It is easily seen, as is done earlier, by means of proper evaluation of orders of magnitude, that again the two first terms are the predominant ones. Then

$$F_B \simeq \frac{\phi_{eff}}{kT} \cdot \frac{\bar{E}}{q} \cdot \frac{1}{\omega} \quad \ldots (17)$$

Equation (17) practically means that the breakdown strength varies inversely to the thickness of the dielectric and decreases linearly with increase in temperature due to the fact that the dominating mechanism is a thermionic injection. The first experimental evidence supporting the above Schottky emission dominated dielectric breakdown has recently been given by Srivastava(54).

Very recently, a theory is proposed by Klein(55) in which breakdown is caused by local chance events, such as a succession of avalanche at one spot. Successive avalanches sustain the growth of space charges, the local cathode field and the avalanche rate. He has shown that when the cathode field becomes large enough to make continuation of avalanching, instability with current runway arises, causing breakdown. According to him the breakdown develops in sequence of stages. The initiative stage increasing the electrical conductivity leading to instability causing current runway and resulting in voltage collapse across the specimen with local melting and vaporization of the insulator under test. This theory tells that breakdowns occur over a range of fields with their chance increasing very strongly with the field. The breakdown is found to occur randomly in space and time and the time to instability on a breakdown event decreases as some exponential function of field.

Klein in this theory has attempted to explain the thickness and temperature dependence of the breakdown field. A decrease of the breakdown field with increasing thickness is shown by him. In very thin insulators, the field at which the breakdown begin to occur is found to be inversely proportional to the thickness of the insulator while for larger thicknesses, the rate of decrease in the breakdown field with increasing thickness becomes smaller. It is clearly implicit in Klein's theory that the temperature affects the development of the breakdown event in insulators and some effects promote and other oppose the development of breakdown. An indirect relation for the case of thermionic emission, when instability requires two successive avalanches is given in which the values for most of the parameters are unknown. He, thus, stated that the temperature behaviour of the electronic breakdown event is quite variable.

The theoretical survey just presented seems to indicate that the electron avalanche is the basic mechanism of breakdown phenomenon. Of all the breakdown theories considered, F-M theory (44) gives the closest agreement with the presently carried out temperature dependence of the breakdown strength data and the thickness dependence data of Agarwal and Srivastava(51,52) on long-chain organic molecular films of fatty acids. The tendency of the breakdown field to follow the $\omega^{-1/2}$ relationship and its weak temperature dependence seems to be the strong evidence for concluding about the nature of breakdown mechanism.

1.2 THERMAL BREAKDOWN THEORIES

Apart from few other processes like electrochemical breakdown, mechanical rupture etc., thermal and electronic breakdown are well known and developed theoretically. In a sense all breakdown are a continuation of the conduction process and these two types of breakdowns definitely start with different mechanism of increasing the electrical conductivity but their behaviour at the end is same i.e. destruction occurs by excessive joule heat. Thermal breakdown involves a temperature rise by joule heat and dielectric loss followed by an increase in conductivity whereas the electrical breakdown is a mechanism due to the direct effect of the electrical field increasing its conductivity involving a number of phenomenon such as avalanche, tunneling and thermionic currents and intrinsic breakdowns as discussed earlier in the preceding section (1.1).

The type of breakdown that has become known as thermal, in general, occurs in two forms. The first one in which joule heat and dielectric loss causes a temperature rise in the specimen with voltage causing destruction at the crtical temperature and the other one widely observed is connected to the thermal instability arising when the joule heat generated by the current flow and the conduction of this heat away to the surrounding from the sample is not balanced. Thermal breakdown occurs at weak spots or uniformly over the whole area of the specimen, which can be made uniform with respect to breakdown by eliminating the weak spots with self-healing, non-shorting breakdowns. Even when the stability does not arise between the heat input and that dissipated, thermal breakdown process is still strongly dependent on the increase of electrical conductivity with temperature. It is evident that the thermal breakdown field depends upon the time application of the field, size and shape of the sample and on the geometry and thermal properties of the electrodes and the ambient medium.

The attempts for the theoretical development of the subject of thermal breakdown were started in 1920 by Wagner(56) and some other workers and the work on this aspect is very adequately summarized and presented in their books by O'Dwyer(57), Franz(19), Whitehead(17), Semenoff and Walther(8). A wide range of comparison of these theories with the experimental observations have been done. Two of the main results of thermal breakdown theories which have been verified experimentally in many cases are that the thermal breakdown field decreases with the increase in the thickness and with increasing temperatures. Klein et al(58) have also proposed a theory and carried out measurements of thermal breakdown field in various thermally deposited thin film systems. However, a detailed discussion of the thermal breakdown theories has not been given here because in the present work, the electronic breakdown processes seem to be dominant. For a detailed and informative review of the whole subject, the reference can be made to the recent review articles of Klein(58, 59) who along with his coworkers has explored the thermal breakdown processes very extensively.

The next chapter reviews in detail the measurements of the properties carried out on thin films including dielectric breakdown studies with particular emphasis.

CHAPTER II

OBSERVATIONS OF DIELECTRIC PROPERTIES OF FILMS

Thin films of dielectrics, a poorly defined yet a major class of materials, have received considerable attention during past few years because of their use in making various dielectric devices. Electrical properties of thin films of various dielectric materials such as oxides, alkali halides, some inorganic and organic polymers and glasses have been experimentally investigated by many workers. Among the electrical properties, most extensively investigated is the dielectric breakdown phenomena in thin dielectric films. This chapter reviews the experimental work done on breakdown in thin films and mainly provides information about the various results related to the temperature dependent behaviour of breakdown field. The studies of dielectric constant, dielectric loss and resistivity of thin films carried out by different workers have also been reviewed briefly here.

2.1 DIELECTRIC BREAKDOWN STUDIES

The quest for practical applications has created interest in the dielectric breakdown properties of thin insulator films. Numerous investigations have been carried out on breakdown phenomena in various thin film systems and are categorised as electronic, thermal and destructive breakdowns. These studies are discussed here under separate heads.

(a) Electronic Breakdown Observations

As is implied by the name 'electronic breakdown' is initiated by the action of electrons forming a highly conductive path through the dielectric. An insulator when provided proper contacts to inject charge carriers, should conduct a current. Recently, an increasing number of authors (60-62) are of the opinion that the low conductivity of organic insulating materials may be caused by carrier injection from the electrodes. If a sufficiently large value of the electric field is applied to metal-insulator-metal structure, the barrier at the low end may be made sufficiently thin to allow an appreciable probability to inject charge carriers into the conduction band of the dielectric resulting in dielectric breakdown. The electrical breakdown strength seems to depend little on breakdown voltage rise time, decreases with increasing thickness and is also influenced by the electrode materials. The breakdown strength decreases slowly with increasing temperatures in the higher temperature region and at low temperatures it is temperature independent. The large scatter in electrical breakdown results is usually due to difference in specimen preparation, local mechanical stresses, weak spots and other experimental circumstances. Among the extensively studied class of dielectrics evaporated films of SiO, SiO_2, MgF_2, CeO_2, Teflon, and thin 'built-up' films of long chain fatty acids deposited by the well known technique of Blodgett and Langmuir(60-62) may be quoted.

There are two main experimental problems in the breakdown investigations. The first is to determine by which of the theoretical criteria the first instability is produced and the second is to investigate the processes occuring in the discharge as it propagates through the dielectric, While there is no clear cut line marking off types of experiment that determine the nature of the instability from those that indicate the mechanism of the discharge, it is perfectly true that investigations of the dependence of breakdown strength on various parameters such as thickness, temperature, etc. give the most straight forward indications of the nature of the instability. It is, therefore, of considerable interest to study the variation of the breakdown field with these parameters. The crystals of alkali halide had been a main part of electrical breakdown investigations. Reference may be made to the recent review article of Klein(58) for these investigations.

The temperature dependence of the breakdown strength of soda-lime glass, silica glass (fused quartz) and crystalline quartz was measured by von Hippel and Maurer(63) using d.c. voltages. For the glass they found that the breakdown strength was nearly constant from liquid air temperature upto room temperature but after that it has been recorded to fall rapidly. For the crystalline quartz the temperature affects the breakdown characteristics throughout the range. The breakdown strength of crystalline quartz has the same positive temperature characteristic as the alkali halides and the breakdown mechanism is probably similar.

The breakdown strength of certain alkali halides as a function of temperature have been measured by some workers(64-66) for various values of the rise time of the applied field. Alger and von Hippel(64) carried out measurements on KBr and showed that at sufficiently low temperatures the breakdown field rises slowly with increasing temperature and is independent of rise time. The breakdown of the alkali halides in this range of temperature was believed to be electronic in nature and was probably due to electron emission from the cathode enhanced by a large concentration of adjacent positive holes which are themselves the product of collision ionization. The work of Cooper and Elliott(67) and Paracchini(68) support this hypothesis. At sufficiently high temperatures, the breakdown field in alkali halides was found sharply decreasing with temperature increase(64). The breakdown was ascribed due to the thermal instability. The breakdown was never found to exceed about 1 MV cm^{-1} in this temperature range. In the intermediate temperature range, the breakdown occuring within a short time interval after application of voltage and the process of breakdown is to be essentially continuous with the low temperature one. Similar results have been found by Konorova and Sorokina(65) on KBr films and by Kuchin(66) while working on NaCl films. Later Hanscomb(69) have also showed that the breakdown of KCl and KCl doped with $SrCl_2$ upto 300^oC to be a continuation of the low-temperature mechanism. This conclusion was in agreement with the results of Watson and Hayes(70) on NaCl upto 350^oC but does not entirely agree with the results given by Cooper, Higgin and Smith(71) for KCl and KCl doped $PbCl_2$. The average breakdown strength of KBr varied from 0.54 to 0.88 MV cm^{-1} as observed by Alger and von Hippel(64).

The current transport through thin insulators have also been extensively investigated and have been reported in numerous reports (72-82). Hartman and Chivian(72) studied the breakdown conduction in thin dielectric films of aluminium oxide (Al_2O_3) sandwiched between aluminium electrodes, for oxide thicknesses less than 35Å using linearly rising voltages from 0 to 10 Volts between temperatures 77^oK and 300^oK. A comparison of their results with Stratton's theory(83) yielded qualitative agreement. Fisher and Giaevert(74) measured the conductance of Al-Al_2O_3-Al structures with an oxide thickness less than 100Å. They observed ohmic behaviour at low voltages and an exponential rise in the current at higher voltages. The observed current in his case was, however, several orders of magnitude lower than the calculated with Holms(84) calculations. Tantraporn(85) has also attempted the similar problem. The comparison of his calculations with the results of Advani etal(75) suggested the necessity of including the image force for an insulator thickness below 150 Å. Pollak and Morris(78) working on similar lines obtained an excellent agreement with Simmon's equations of tunnel current (86) at 300^0K. Korzo(87) have also investigated Al_2O_3 films in different thickness ranges giving a number of emperical formulae for thickness dependence of the breakdown field. A power dependence of the type $F_B \alpha \omega^{-\alpha}$, with $\alpha = 0.45$-0.85 has been obtained in the range 800-2000 Å. The breakdown strength of plasma oxidised Al_2O_3 was recorded to be temperature dependent as shown by Nicol(88).

Electron transfer through ideal, single crystal films of vacuum cleaved mica was studied by McColl and Mead(80). The current-voltage data on 30 and 40Å thick films were in good agreement with the Stratton's theory(83), however, at higher voltages (greater than the barrier height), the magnitude and the functional dependence of tunnel current departed markedly from the theory. The temperature dependence of the tunnel current was also studied by several workers (73,76,77), although, a greater temperature dependence than that predicted by the theory is observed.

Thin silicon dioxide films, usually grown either thermally or anodically on silicon substrates and having an evaporated metal counter electrode have been extensively studied during recent past. The electrical characteristics of silicon-silicon oxide interface were reviewed by Lamb(89) and Sze(90). The high field conduction properties of this structure were interpreted by Lenzlinger and Snow(91) as being due to Fowler-Nordheim emission(92). The variation of the electrical strength of amorphous silicon oxide films with temperature was studied by Korzo(93) in the temperature range between 80°K and 323°K for relatively thicker films(400Å-5000Å). The electric strength was found about 10 MV per cm. for 300Å thick samples and 20 MV per cm. for 80Å thick samples. The temperature dependence of the breakdown field was observed to be linear having a flat maximum between 0 and 50°C for 2000 Å thick specimens but temperature effect was negligible for low thickness samples. Korzo(94) also studied pyrolytic SiO_2 films in the temperature range (72-233°K) and found a nonlinear dependence upon temperature and film thickness. Thermally grown SiO_2 layers were studied by Fritzsche(95) and Pratt(96) as a function of temperature, layer thickness etc. The breakdown field was again found of the order of 10 MV/cm. The d.c. breakdown strength decreased slowly as the temperature rose from -20°C to 100°C. Pratt(96) has shown that it varies as $d^{-0.66}$ for films upto 10,000 Å.

Electrical conduction and breakdown studies in thermally evaporated SiO films formed between metal electrode films have also become a subject of vast researches since last one decade. Siddall(97) and Chaiken and St.John(98) studied experimentally destructive breakdown in Al-SiO-Al capacitors but made no attempt to relate their results to any theory of breakdown. Hartman et al(99), Schenkel(100) and York(101) made only passing references to breakdown strength. However, these authors agree that the applied field should be ranging between 0.4 to 4 MV/cm for dielectrics of thicknesses 1000 to 20000 Å. Siddall(97), however, found that dielectric strength is greater if SiO is deposited slowly. Budenstein and Hayes(48) who have done an extensive work on dielectric breakdown phenomena in thin films, undertook the investigations on Al-SiO-Al capacitors and studied destructive breakdown using transmission electron microscopy and electron diffraction. Purely electrical breakdown has been observed with the breakdowns originated at inhomogeneties in the dielectric. Self-healing breakdowns were used in order to eliminate weakspots and to take a large number of tests on a single sample as self-healing breakdown does not cause a permanent short circuit but a pinhole through the dielectric along the breakdown path and a larger hole in the metallic film electrode(50). Electrical measurements carried out (50) revealed two well defined, polarity sensitive threshold voltages, one for the 'onset' of breakdown and the other for cessation of breakdown. The onset breakdown voltage was found to decrease with increasing temperatures in the range ($77^{o}K - 380^{o}K$) and vary approximately as $\omega^{-1/2}$ in agreement with the Forlani-Minnaja's theory(44). The voltage threshold for the cessation of breakdown was temperature independent.

Nishimura et al(103) investigated the breakdown characteristics of SiO film and found it to be affected by gas adsorption and depending upon deposition conditions. The dielectric breakdown voltage was found increasing with the lowering of pressure during deposition. Inagaki and Nishimura(104) later studied the large effect of the dielectric breakdown voltage characteristics through gas adsorption associated with the deposition conditions. Inagaki et al(105) also used Al-SiO-Al type film capacitors and showed that the breakdown voltage increases with slower deposition rate, with thinner films and, with decreasing pulse width. They, however, proposed the avalanche mechanism as the basis of breakdown in SiO films. The dielectric strength is very little dependent upon temperature and the nature of breakdown was stated to be non-thermal.

Budenstein along with his coworkers(50) later studied thin films of some inorganic dielectrics (SiO, MgF_2, CeO_2 and Teflon) evaporated thermally between temperatures 80^{o} and $380^{o}K$ and found all of these independent of prebreakdown a.c. and d.c. conduction. The threshold field for the 'onset' of breakdown was found independent of temperature and varying with film thickness as $\omega^{-1/2}$. The cessation voltage for breakdown was found typically between 10-20 volts for all the samples under test. They observed that light is emitted during destructive breakdown and suggested that breakdown conduction is due to gaseous arc. In another report(49) Smith and Budenstein presented their studies of d.c. conduction and breakdown phenomena in thin film capacitors of CaF_2, MgF_2, NaF and LiF. A decrease of breakdown field (F_B) was found for temperatures -200°C to 100°C and the breakdown field found of the order of 10^6 V/cm. Similar to the results on SiO of Budenstein and Hayes(48) the voltage threshold for the cessation of breakdown was $\simeq$15V which is again thickness and temperature independent. In general Budenstein's work on dielectric breakdown is in conformity with Forlani-Minnaja's theory(44).

Recently, an **extensive** study of dielectric breakdown and electrical conduction in thermally grown SiO_2 films on silicon was carried out by Osburn and Ormond(106, 107). These authors found their breakdown characteristics to be varying with a number of parameters such as temperature, oxide thickness, electrode thickness, sample preparation etc. For thin aluminium electrodes, they recorded only the initial, self-healing breakdown voltage and the final destructive breakdown voltage ignoring any intermediate breakdown event. The maximum breakdown strength was found to increase slightly (by about 8%.) with increasing temperature in the range -196°C to 300°C and vary with thickness as $\omega^{-0.21}$ below 800 Å and constant from 1000 to 2000 Å. The initial self-healing breakdown were largely independent of materials and measuring parameters such as electrode thickness and oxide thickness etc. On the basis of their experimental findings, they have established that the breakdown mechanism with these films is electronic in nature rather than thermal.

The dielectric breakdown of polymers have been studied very extensively and reviewed by Whitehead(17) and by Mason(108). Low field conduction in polymers has been interpreted as ionic or electronic depending on the polymer in question and on other conditions such as temperature etc. Ieda etal(109) measured the temperature dependence of the low field conductivity of low density polythene, both pure and with metallic salts as impurities. Seanor(110) investigated the conductivity of Nylon-66 from room temperature upto 150°C and found protonic conduction in the upper portion of the temperature range while electronic conduction dominated in the lower part. Taylor and Lewis(111) investigated conduction in polythene terephthalate and polyethylene without any excitation of carriers and using current-voltage measurement techniques. They found a long term decay of current for a steady applied voltage and their results were explainable by Schockley's theory(42,112).

The breakdown strength as a function of temperature is recorded generally of the same form for all the polymers, that is, almost constant at low temperatures and falling-off at higher temperature(44,113,114). Later, extensive investigations carried out by Riehl, Baessler, Hunklinger, Spanning and Vaubel(115) who developed a technique of non-destructive breakdown study similar to the self-healing breakdowns observed by Klein(102) in SiO. Near 4K, the prebreakdown current was identified with Fowler-**Nordheim** emission of electrons from the cathode over a barrier of 1.8 eV which agrees reasonably well with the values obtained by Lilly, Lowitz and Schug(116) for thermionic emission at higher temperatures showing the electrical nature of the breakdown observed.

One of the most interesting recent dielectric breakdown studies is on thin 'built-up' Langmuir films of some soap metals. Interest in these studies have been stimulated because of their promising use in device applications and because of certain advantages with these films such as easy reproducibility, uniformity of layers and good thermal stability etc. Porter and Wyman(117) studied breakdown in these films having different number of layers. The films were covered with a drop of mercury and were subjected to a variable d.c. voltage with a galvanometer in series. With films of higher thickness there was no observable deflection in the galvanometer until a certain critical breakdown voltage was reached. Race and Reynolds (118-120) also carried out similar type of measurements on barium stearate films. The voltage was varied from 0.01 volts up using a fine potentiometer and measured by a high resistance voltmeter. For a.c. measurements the voltage was supplied by a beat frequency oscillator. The output voltage was controlled by a potentiometer on the oscillator panel and was measured with a vacuum tube voltmeter. They found that the dielectric strength measurements were not very reproducible even after taking considerable care to prevent the inclusion of dust in the multilayer films. Holt (121) measured the maximum dielectric strength of multilayer films and found its value varying from 1.3×10^{6} V cm^{-1} at 225 Å to 2.6×10^{6} V cm^{-1} at 3700 Å.

A knowledge of the effect of the temperature on the breakdown strength in thin 'built-up' films of barium stearate etc., which have been studied by the author in the present work can be of considerable importance in theoretically understanding the mechanism of dielectric breakdown. Equally important are the thickness dependent studies in these films in determining the breakdown mechanism. Recently, Agarwal and Srivastava(51)have studied systematically the thickness dependence of dielectric breakdown in barium stearate in the thickness range (25-2000 Å) at room temperature (298°K). For the range studied, the breakdown strength was found to be a power dependent function of thickness varying as $d^{-\alpha}$, d being the thickness of the dielectric film. For larger thicknesses(corresponding to 10 to 80 layers) the results were in very good agreement with the avalanche breakdown theory of Forlani and Minnaja(40) which predicts the value of α to be 0.5. In the lower thickness range (1-10 layers), the value of α was found to be about 1.00 for all the films studied(51,54). A.C. breakdown studies (122) of barium stearate film have also been carried out as a function of frequency, in the range (10-200 KHzs) and thickness in the range (100-1500 Å). All the measurements were taken at room temperature (298°K). The a.c. breakdown voltage was found to be increasing with increasing frequency and with the thickness, varying as $d^{-\alpha}$ with $\alpha = 0.68$. Based on their measurements, they have concluded that the breakdown processes in these Langmuir films are electronic in nature rather than thermal. In all this work, the authors, however, have not studied the temperature dependent behaviour of the breakdown field in 'built-up' films, as attempted in the present work (Chapter VI and VII).

(b) Thermal Breakdown Observations

In insulators, thermal breakdown has been observed both at weak spots and uniformly over the specimen. Klein and his coworkers (2,58,59,123-128) have done very extensive work to describe thermal breakdown processes in thin films, particularly on silicon oxide films and a number of papers have reported in the literature concerning their thermal breakdown studies.

Klein and Gafni(2) studied d.c. breakdown in SiO films at room temperature eliminating the weak spots of the specimen and found a good agreement between their theoretical and experimental values of maximum voltage. SiO specimens (4100 Å thick) cleared of weak spots were studied by Klein and Lisak(123) in the temperature range (4.2°K to 415°K) and a quasi exponential rise in the current with temperature was observed above 70°K as predicted theoretically (2). Recently, Brestechco and Klein(124) found a slight decrease in the magnitude of the d.c. thermal breakdown field in vacuum as compared to that at atmospheric pressure. For a sample of thickness 4.5×10^{-5} cms, the breakdown strength was recorded to be 2.9 MV/cm and 1.5 MV/cm for 1.5×10^{-3} cm. thick specimen of silicon oxide at room temperature.

A.C. thermal breakdown was also reported by Klein and Lavanon(125) on SiO samples in the frequency range (10 to 50,000 c/sec.) and the breakdown voltage was found to be frequency independent upto 1000 Hzs and then decreasing linearly with frequency owing to dielectric losses. A.C. breakdown strength was, however, found to be 10-20% larger than the corresponding d.c.ones. Klein and Burstein(126) carried pulse breakdown studies for 5×10^{-5}cm. thick SiO films and found a good agreement between the observed and calculated values. The study of the switching phenomena in thin films has also been undertaken by Klein and his results on switching are reviewed in his paper(59). For detailed information regarding thermal breakdown results and processes, the reference may be made to an excellent review article of Klein(58).

(c) Destructive Breakdown Observations

Destructive breakdown phenomena has been a subject of vast researches since last two decades and a considerable amount of work has been done. The destructive breakdown which is rather a complex process, is influenced by temperature rise, by melting process, by drastic reduction of the potential barrier at the metal-dielectric interface (junction) and possibly by large current densities which are responsible for the event. The electrodes usually melt or evaporate forming some kind of conducting bridge, thus leading to the shorting of electrodes.

Klein and his coworkers(2,125-128) studied in detail the mechanism of destruction on self-healing thin films of SiO. Various types of breakdowns were observed by them which were distinguished as 'single hole', 'popagating' and 'maximum voltage' breakdowns. The first two were attributed to localised flaws in the dielectric destroying a small and large area of the specimen, respectively and the third was regarded as bulk property destroying the whole capacitor, simultaneously. Single hole breakdown is associated with relatively large valued series resistors and small applied voltages and often occured at fields below 1 MV/cm is followed by rapidly increasing breakdown with increasing voltage as was observed by Siddall(97). In all this work self-healing breakdowns were used in order to eliminate weak spots and if the electrodes are thin enough, a small hole in the dielectric and a larger hole in the electrode were observed(2). If the electrodes are of dissimilar thickness, a pit in the substrate, a small hole in the dielectric and a large hole in the counter-electrode have been reported(128,129). When breakdown occurs, the voltage decreases to a minimum during the discharge and then since the breakdown is self-healing, the capacitor recharges from the supply through the series resistor in the circuit. Klein assumed (128) that the destruction occuring during the breakdown was due to discharge of the energy stored in the SiO capacitor. If the applied voltage is further raised or the series resistor is reduced, propagating breakdown was recorded. Klein observed that the propagating breakdowns occur at adjacent sites, probably, because the dielectric is weaker at the hot perifery of the previous breakdown. This occurs in three stages. In the first stage, a conducting channel is formed in the dielectric due to high electric field, in the second stage, the stored charge of the sample discharges through the channel triggering to the third stage of propagation of the breakdown from power sources leading to the destruction of the film.

Extensive investigations of the destructive breakdown in thin-films have recently been reported by Budenstein and his coworkers(48-50) in their pioneering work. Unlike, in the work of Klein and Gafni(127), Budenstein et al made use of SCR circuit. According to them the mechanism involved here is governed by a gaseous arc. Budenstein and Hayes(130) on the basis of their experimental findings, concluded that the classification of breakdown, proposed by Klein and Gafni, is purely phenomenological. According to them, maximum voltage breakdown represents an ultimate dielectric strength in a special circuital context but the destruction occurs through many single breakdowns. The sides of the region of destruction increases with the area of the capacitor for a given thickness of the dielectric and the breakdown is, essentially, electrical rather than thermal in nature. However, the phenomenon of destructive breakdown is still in a state of confusion and is not fully understood in all details.

2.2 DIELECTRIC CONSTANT MEASUREMENTS

A study of the dielectric constant of thin insulators like 'built-up' molecular films is of potential importance for the development of thin film capacitors. The dielectric constant of thin films was measured by a number of workers in different thickness and frequency ranges. The temperature dependence data of the capacitance is, however, scarce.

Early studies of dielectric behaviour of 'built-up' stearate multilayers were carried out by Porter and Wyman(117), Race and Reynolds(118-120) and Zahl and coworkers(131). Porter and Wyman(117) measured the capacitance of the 'built-up' multilayer films by placing a small drop of mercury which forms the upper electrode of the capacitor. Film of organic layer was deposited on the aluminized slide forming the lower electrode of the capacitor.The capacitance was measured at radio frequencies using a radio frequency bridge and was found almost independent of frequency. The thickness dependent behaviour of the capacitance was also studied by these authors and the capacitance was found to decrease with thickness. The average value of the dielectric constant of stearate films as reported by these authors is approximately 2.5 which is very close to the bulk phase value. The dielectric constant obtained was varying from 1.9 to 3.5 for the thickness range 175Å to 3525Å (i.e. 7 to 141 monolayers).

The capacitance measurements of 'built-up' barium stearate films were also carried out by Race and Reynolds (118) over the frequency range 40-10^6 Hertzs by means of special guarded bridge(119) using small area probe method. From these measurements, dielectric constant (K) and dielectric loss (tanδ) of the films were calculated using the equivalent parallel circuit(120). They found that the dielectric constant was independent of the film thickness and also with the frequency upto 10^6 Hzs. However, no temperature dependence behaviour has been given by these authors.

Buchwald, Zahl and their coworkers (131) made an attempt to measure the insulating properties of stearate films by immersing multilayer coated metal rods into conductive salt solution. A decrease in capacity was observed with increasing number of layers. However, they found atleast two-fold variation in apparent dielectric constant which were influenced by the choice and concentration of the electrolyte. These authors have not attempted temperature dependence study of the capacitance.

Recently, Handy and Scala(132) investigated the electrical properties of barium stearate films using the evaporated metal electrodes rather than mercury drops to sandwich the organic films deposited on aluminized slides. According to these authors, the evaporated metal electrodes lead to a higher incidence of shorts through defects in the films but they provide a realistic test of film uniformity and of the practical utility of Langmuir films for use as ultra-thin insulating films. They found the dielectric constant to be varying from 2.1 to 4.2 with an average value of 2.5, which is evidently same as reported by earlier workers on stearate films. The capacitance was also measured as a function of frequency and a slight change in the capacity with frequency was observed.

Drexhage and Kuhn(133) who have studied the capacitance as a function of thickness of cadmium stearate films have shown the constancy of the dielectric constant with thickness. Mann and Kuhn(134) calculated the dielectric constant of monolayers of cadmium salts of fatty acids of different chain lengths containing 18-22 carbon atoms.The capacitance was measured with a L-C precision bridge of Rhode and Schwarz at a frequency of 1000 c.p.s. and the dielectric constant was found to be increasing with decreasing chain length. According to Beck(135), the capacitance of the fatty acid monolayers is reproducible within 3%. . Recently, Holt(121) have also shown that in general the standard deviation in capacitance per unit area of each film being as low as 3%., that is, of the same order as the accuracy to which the areas of the electrodes can be measured. He has not given dependence of capacitance on temperature but have shown no variation in capacitance with frequency. Horiuchi et al.(136) have also carried out similar measurements on barium stearate films and shown independence of the capacitance with the frequency over a wide range (1KHz-1MHz). The dielectric constant was calculated from the capacitance of barium stearate films equal to 2.5 as has reported in earlier studies.

Recently, Khanna and Srivastava(137) have also carried out measurements of capacitance of 'built-up' films of some fatty acid salts, as a function of thickness and thereby, calculated the dielectric constant of these films. For a monolayer of barium stearate, they have observed a value 1.62 while for thicker films, the dielectric constant was found to be 2.72. This value of dielectric constant is evidently is in good agreement with bulk phase value. These authors have not carried out temperature and frequency dependence of the dielectric constant.

2.3 DIELECTRIC LOSS MEASUREMENTS

Dielectric loss is essentially a bulk property of a substance and is generally measured simultaneously with the measurement of the dielectric constant. The dielectric losses in anodic oxide films have been studied extensively and are reviewed by Young(129). These films generally display a constant loss factor at audio frequencies. A little work has been reported of the dielectric loss in thin films as a function of frequency and temperature (138,139). At higher temperatures above about 200°C, depending on the capacitor materials, the diffusion of the film electrodes into the insulator film is significant producing a rapidly rising dielectric loss(138). The loss in the evaporated film capacitors of ZnS, MgF_2 and SiO is found to increase with frequency in the range 10 to 10^4 Hzs(140). The dielectric loss in ZnS films exhibits peaks at about 210 and 475°K which correspond to activation energies of 0.16 and 1.18 eV, respectively. Weaver has also studied the dielectric properties of thin films of alkali halides (CaF$_2$, LiF, NaF, NaCl, RbBr and MgF$_2$) and has reviewed his work in several articles(141-144). Capacitance and dissipation factor measurements over a frequency range from 0.01 cps to 100 Kcps showed that at room temperature the dielectric losses decreased steadily with aging time after deposition and both i.e. dissipation factor and the capacitance increased toward the low frequency range. Marked increase in the capacitance and loss factor was reported as a result of adsorbed moisture, even for water insoluble MgF$_2$. However, this type of losses were not observed in bulk single crystals (145). Weaver suggested that the basic loss mechanism in alkali halide films are due to the excess vacancy concentration and the later observations(146) have shown that the losses are produced by the motion of cation vacancies. If these vacancies are assumed to condense at the intercrystalline boundaries, their observed rate of condensation is in good agreement with the calculated rate for anion vacancies, using the activation energies obtained from independent measurements.

In single crystal epitaxial films, the losses are expected to be lower. The results (147) for (100) epitaxial LiF films deposited on an epitaxial silver film deposited in turn on a rock salt substrate confirm this conclusion. Hirose and Wada(148) measured the dielectric losses in SiO films from 10^{-2} to 10^{7} cps and observed a loss peak at 0.1 cps. This peak corresponds to an activation energy of ~0.4 eV, a value also obtained from the d.c. conductivity data. Recently, Budenstein etal(48,50) have also carried out dielectric loss measurements of some thermally evaporated ionic films as a function of temperature. Peaks are found for the dissipation factor in CeF_3, CaF_2 and CeO_2 films and these peaks increases as temperature increases. The behaviour of the variation of capacitance and dissipation factor with temperature is found similar in MgF_2 films and in general loss increases as temperature is higher.

The dielectric constant as well as the dielectric loss measurements were also made by Race and Reynolds(118) for 'built-up' stearate films and it was found that these are the two independent properties of the films. The plot of the dielectric loss against frequency show larger deviations. However, these deviations appear to be random and show no dependence on thickness and frequency. The order of magnitude of $\tan\delta$ measured was low(than 0.001, with a standard deviation of 17%) with those obtained by Haskins and his coworkers(149). Assuming equivalent parallel resistance and capacitance of the films, their data indicate a two-fold variation in dielectric constant and 15-fold variation in $\tan\delta$ as a function of thickness and the order of magnitude of tanδ in their case was 1000-10,000 times higher than the value obtained by Race and Reynolds(118). The wide difference in their values was caused by the electrolyte in which the film was immersed.

Recently, Holt(121) and Handy and Scala(132) have carried out detailed studies of the dielectric behaviour of Langmuir films. Holt(121) also measured the loss angle (tanδ) for the thickness range (225Å-3700Å) and found that the values dropped from 0.2 at 225Å to 0.006 at 3700Å showing the standard deviation of 25% . The variation in loss angle with frequency followed normal thin film behaviour. Handy and Scala(132) showed the variation of dissipation factor with frequency. They observed a slight maximum near 700 Hzs and interpreted suggesting the presence of weak polar adsorption mechanism with a characteristic relaxation time of 0.03 m sec. At higher frequencies (> 10 KHz), the measurement uncertainty in the dissipation factor become comparable with the observed values. However, these authors have not studied the temperature dependence of the dissipation factor in Langmuir films.

2.4 RESISTIVITY MEASUREMENTS

Thin anodized as well as thermally oxidized films of some inorganic materials and some organic polymer films are generally good insulators with high resistivities. The resistivity measurements of thin films have been carried out by several workers on various film systems. Zahl and coworkers (131,149) have measured the resistivity of organic multilayer films and an increase in resistance was observed with increasing number of monolayers. However, there was several orders of magnitude variation in resistivity which was influenced by the choice and concentration of electrolyte. Small area probe measurements using water or mercury droplets were more successful. The variations observed in resistivity values were generally ascribed to inhomogeneties or voids in the films. Porter and Wyman(117) also measured the resistance of stearate 'built-up' films and found that resistance increases with the increase in thickness. The values of resistance at 1 MHz were definitely less than those at the lower frequency. Recently, Handy and Scala(132) have also measured the resistivity of barium stearate films at low voltages (below 50 mV) where the conduction behaviour is ohmic. They plotted the resistivity against thickness and found that the points were approximately uniformly distributed over a certain limited area of the plot. For a given thickness, the upper limit of resistivity was corresponding to those layers which possess the smallest fraction of voids. They found that there was a wide range of variation of resistivity values for the same number of layers which supported the contention that the organic films possess porous structure. They also concluded that at low thicknesses, the resistivity values were the characteristic of the oxide layer as the fractional area of the oxide film remain in direct contact with the upper electrode. Handy and Scala then arrived at some general conclusions that the reproducibility of the electrical properties of the films was poor, apparently because of voids and inhomogeneities in the organic insulating films.

The next chapter describes the fundamental characteristics of monomolecular films, on which, is based the development of the well known Blodgett-Langmuir technique of 'building-up' molecular films of metalic salts of some long chain fatty acids, studied in the present work.

CHAPTER-III

MONOMOLECULAR FILMS

Insoluble monomolecular films on liquids have been studied for many years because of their possible use for both technological and scientific purposes. For example, films which reduce evaporation losses at water surfaces, are of particular interest. In these processes, the ultimate film, which is only one molecule thick, plays the most important role. Such a film is known as monomolecular film or monolayer. The monomolecular spreading on liquids is one of the most fundamental phenomena in the realm of physics and chemistry of surfaces. A wide occurrence of insoluble monolayers of many organic substances is now well known (Adam,1941). Monolayers at a liquid-gas interface can be controlled, manipulated and examined under far better conditions. That is why, the monolayer at the water-air interface has been extensively studied in the pioneering work of Rayleigh, Langmuir, Adam, Rideal, Harkins and other workers providing much basic information on such monolayers. Here, particular stress has been given to the understanding of monolayer properties because the 'built-up' films which have been studied extensively in the present work, have been deposited simply by transfering these monolayers on to solid surfaces.

This chapter provides information about the surface tension phenomena and spreading of organic substances on water. The interpretation given by Lord Rayleigh of Pockel's observations on monolayer spreading of olive oil on clean water surface and the effect of oily contamination on surface tension of water has been discussed in detail. The existence of short range forces and the mechanism of monolayer spreading on water surface have been discussed in brief. Some fundamental information about individual molecules, such as the length of the molecule obtained by these experiments are also described.

3.1 SURFACE TENSION AND MONOMOLECULAR SPREADING

(a) Surface Tension of Water

Some amount of work has to be done in bringing the molecules from the interior of the liquid to its surface due to the intermolecular cohesion. This work done is stored as free energy of thus created new liquid surface. The free energy, thus stored per unit area of this newly formed liquid surface is termed as the 'surface tension' of the liquid. It was supposed for a long time that a liquid surface resembles a 'stretched skin under tension' but it is not so and thus the term 'surface tension' is a misnomer. However, the two definitions of the surface tension that it is the force (dyns/cm) acting normal to a unit length in the liquid surface and the other stated as the free energy per unit area of the liquid surface.

are equivalent.

The surface tension of water is lowered due to its oily contamination. The amount of this lowering was first measured accurately by Lord Rayleigh(150). He found that surface tension is reduced by 21 dynes/cm when 0.91 mg.of olive oil was added to a surface covering an area of 555 sq.cms.of water surface. He had also estimated the average thickness of thin oil film on water to be about 16Å, with the help of area-density method, to be described in section 3.1(c).

Using a very simple apparatus, later, Miss Pockels(151) had made a detailed and systematic experimental study of the effect of oily contamination on the surface tension of water. The apparatus used by her was consisting of a long narrow trough filled to the brim with water and two rectangular metal strips called 'barriers', which rested across the long edges of the trough. These movable barriers were used to sweep-off the impurities of the surface and a desired area of the surface could be selected by drawing-out or drawing-in these barriers across the long edges of the trough. The desired area of water surface, thus enclosed between the barriers, could now be contaminated by placing a small drop of olive oil on the water surface. This olive oil can not leak through the barriers because they touch the water surface all along. The contaminating oil remains confined on the large or small area of the water surface by pulling-out or pulling-in the barriers along the long edges of the trough.

Miss Pockels(151) observed that the surface tension of water remains unchanged if no excess oil in the form of small drops remain on the contaminated water surface permanently. When a very small amount of olive oil is added to contaminate fairly large area of the water surface. The constancy of surface tension of the contaminated water surface(equal to that of a clean water surface) was found upto a certain critical area and below this critical area an abrupt fall in the surface tension was noted when the area of this contaminated surface was reduced by gradually drawing in the barriers. This critical area depend upon the amount of olive oil placed on the water surface. Pockel's also observed that if the amount of oil is less than that enough to give a critical thickness of about 10Å to contaminate a given area of water surface, the surface tension of water remains unaltered but the surface tension of the water surface falls rapidly as the amount of olive oil is increased beyond this limit. Using area-density method (sec.3.1.,c), the amount of olive oil enough to contaminate the critical area or to give the critical thickness of 10Å can be estimated if the density of the olive oil and the contaminated area are known.

(b) Monomolecular Spreading of Olive Oil on Water Surface

Few years later, Lord Rayleigh(152) repeated many of Pockel's experiments to confirm her interesting observatioms outlined above. He suggested that when olive oil is placed on the water surface, it spreads out forming a monomolecular layer on the surface and molecules of oil in the critical area observed by Pockels remain closely packed just touching each other. These ingenious suggestions of Rayleigh thus originated the fascinating subject of monomolecular films. The thickness of the films comes out to be nearly equal to known length of the molecules as observed by Lord Rayleigh(152). But his detailed explanation of Pockel's observations, as has been given in next paragraph, clearly shows that the monomolecular theory rests not merely on a numerical coincidence but is based on far firmer foundation of the idea of 'tangible floating molecules'.

All of the Pockel's observations can be explained very well in the light of Rayleigh's suggestions as follows. The molecules in a drop of olive oil, when placed on the water surface, spread out quickly forming a monomolecular layer on the water surface. The cause and the mechanism of the spreading phenomenon is described in Sec.3.3(a). Obviously, the area of the water surface available for the spreading of oil molecules can accommodate as many of them as can be closely packed in a completed monolayer. The number 'n' of the molecules spread on the water surface is given by the area of the available water surface divided by the cross-sectional area (sec. 3.3(c)) of the molecule. If the number of molecules in the amount of the oil placed on the area of water surface is greater than 'n', the 'n' molecules will spread to form a close packed monolayer and the excess oil in the form of lenses of considerable thicknesses is left permanently on the water surface. Conversely, if the available number of oil molecules is less than 'n', all the molecules will spread out on the water surface leaving no excess oil in the form of lenses on the surface. The spreading of the oil in this case will be incomplete in the sense that the molecules in the spread layer do not touch each other and are free to move about on the water surface relatively independently. In the former case, the molecules in the layer are closely packed touching each other over the whole water surface leaving no excess space on the area for the molecules to move about and hence the spreading is complete in the former case.

It is thus clear from the above that in Pockel's experiment the spread oil molecules do not form a complete closed packed molecular layer in areas greater than the critical area. In all these stages of compression of the monolayer by drawing-in the barriers which are gradually reducing the area of the contaminated water surface, the oil molecules do not touch each other and move about on the surface due to the excess space available. If the area in which the spreading of oil takes place is greater than the critical area the molecules remain sufficiently for apart from each other and therefore the electrostatic repulsive forces between the molecules do not come into play. Hence, no work is required to be done in compressing the monolayer by barriers in diminishing the area of the contaminated water surface upto the extent of the critical area. The free energy of the underlying water surface will, therefore, remain intact and the surface tension thus does not change upto the critical area. As soon as area of the contaminated water surface equals the critical area on compression by drawing-in the barriers, the molecules in the compressed monolayer becomes closely packed and just touch each other. The mutual electrostatic repulsion between the molecules at this stage, comes into play rather abruptly and the first resistance to compression arises due to which the molecules start experiencing an outward pull tending to spread them. This outward force exerted (because of the mutual repulsion between the molecules) on an element of unit length in the monolayer is known as 'surface pressure' (dynes/cm) of the monomolecular film. For compressing the monolayer, furthermore, even slightly, some work is required to be done at this critical stage when the intermolecular repulsion just comes into play and the required energy for this work comes from the free energy of the underlying water surface. Therefore, when the area of the contaminated water surface is reduced, below the critical area, the surface tension of water falls abruptly. From the energy considerations Adam (153) has shown that the reduction of surface tension is equal to the surface pressure of the film. Obviously, the critical area value, will depend on the amount of oil placed on the water surface. Hence, the critical area having closely packed molecules just touching each other will be greater if the amount of the oil or the number of available molecules is greater.

In the experiments described above, the amount of the contaminating oil was kept constant and the area of the contaminated water surface was varied while in the Pockels experiments on surface tension, she kept area of the water surface constant and contaminated it with increasing amount of olive oil. Here, so long as the area of the water surface is contaminated with an amount of oil less than one which contain 'n' molecules (Sec.1.1.b), the molecules in the spread monolayer will not be closely packed. The surface tension does not change as the intermolecular repulsion at this stage does not come into play. The spread monolayer become closely packed when this area of water surface is contaminated with just 'n' molecules of olive oil. When the amount of oil is slightly increased to this critical limit, the intermolecular cohesion just comes into play and therefore the surface tension falls rapidly. The average thickness of the monolayer in the critical stage, as observed by Pockels in her experiments was nearly 10 Å. In this way all the Pockels observations can be explained following Rayleigh's suggestions.

A simple interpretation of the fall in the surface tension due to the oily contamination of its surface can also be given as follows. The surface tension of water with a clean surface is determined by the cohesion or attraction between its surface molecules and those lying underneath. Because of this attraction, the surface molecules experience an inward pull in a direction perpendicular to the surface because of the attraction. When oil drop is poured on the surface cohesion or attraction between the surface water molecules and those lying underneath is opposed by the adhesion or attraction between the oil molecules and the water molecules in the surface, as a result of this, the inward pull on the surface water molecules is bit reduced and consequently the surface tension of water with contaminated surface is less than that of the clean surface. The reduction in surface tension will obviously depend on the adhesion or attraction between the contaminating molecules and the water molecules. The greater is the adhesion, more will be the reduction in the surface tension and vice-versa. But, in case adhesion equals the intermolecular cohesion (between the water molecules itself), the interfacial surface tension would vanish and the contaminating molecules would become completely miscible with water molecules and all of them slowly go into the solution with each other.

Raleigh's monomolecular theory (152), thus explains all the experimental observations in a most remarkable way. His ideas now seem to be absolutely indispensible for interpreting the basic phenomena of surfaces. This phenomenon of monomolecular spreading has come to stay as most fundamental one in the field of Physics and chemistry of surfaces(153).

(c) Spreading of other Organic Substances on Water: Experimental Evidence for Monomolecular Spreading

As has been shown above Rayleigh's monomolecular theory(3) provided a powerful tool for interpreting the basic surface phenomena which could be studied experimentally by using an extremely simple apparatus, which was first used by Pockels. In fact Pockel's application of movable barriers to confine films to compress them or to remove any undesirable surface contamination laid the foundation for nearly all the work with films on liquids (153-155).

It was realized from the Rayleigh's successful explanation of Pockel's observations that a close study of monomolecular layers would yield the fundamental informations about individual molecules e.g. length of the molecule, their cross-sectional area, the strength of intermolecular cohesion and of the polar group etc. The promise of glimpse into the fundamental aspects of individual molecules with the use of very simply apparatus has constantly inspired the extensive experimental investigations of the monomolecular films. As the monomolecular films can be regarded as a two dimensional matter existing in all the three states, solid, liquid and gaseous (153), a theoretical study of these monomolecular layers has also been very attractive. Thus, investigations in the field of monomolecular films are most interesting and fascinating ones.

The mechanical, electrical, optical and chemical properties of molecules in an oriented array had already been revealed by a large number of experimental methods which characterize monolayers and have contributed much information about the shape and size of molecules. All, of course, depend on the formation of a suitable film for study. The successful organic substances known for spreading as monomolecular layers on water surface are fatty acids, alcohols, esters, ketones, sterols, dyes, chlorophyll, proteins etc. (153-157). Among these substances most thoroughly investigated are the long straight chain fatty acids e.g. palmitic acid, stearic acid etc.(153). Layers of these acids have a molecular structure consisting of a long hydrocarbon chain with a nonpolar (hydrophobic) methyl(CH_3) group at one end and a polar (hydrophilic) functional carboxylic (COOH) group at the other one. The parent hydrocarbons do not spread to form monolayers but the presence of this polar group at the end of long hydrocarbon chain causes the spreading of these fatty acids. The mechanism of spreading is described in Sec.3.3(a).

Devaux(158) studied a number of materials with simple but elegant experimental method and noted that the behaviour of the films is sometimes as solid and sometimes as liquid. Hardy(159) found that oils which do not contain polar functional group do not spread in the same way as the animal and vegetable oils.

The first studies on the fatty acids were made to confirm the monomolecular spreading of these acids on water surface. Langmuir(160) justified the monomolecular spreading and the formation of monolayer on water surface by estimating the thickness of the spread film using simple area-density method. If a spread film occupied an area 'A' of the water surface and 't' is the average thickness of the film, A x t = V is, obviously, the volume occupied by it. This volume V multiplied by the density d of the film, gives the mass m of the material of the acid spread. From a knowledge of A, d and m, the average thickness of the film t can easily be estimated. When the area A is reduced down to the critical area, the corresponding value of t now obtained will be equal to the length of the molecule. This is so because the molecules stand perpendicularly on the water surface due to the close packing of the molecules. Thus, the length of the molecule in monolayer could be estimated from experimentally determined critical area and the corresponding amount of acid spread. A check of the basic assumption of monomolecular spreading of the fatty acid could now become possible by tallying the length of the molecules thus measured with the values of the chain length obtained by other methods e.g. X-ray diffraction measurement of the chain length in bulk crystals of the fatty acid. Thus, the estimated thickness of fatty acid monolayer on water surface by the above discussed area-density method, are in agreement(161,162) with their corresponding chain lengths in bulk, studied by X-ray diffraction (163). This work thus supports the Rayleigh's hypothesis(152) of monomolecular spreading and has established that the spreading of fatty acid on water is monomolecular in nature. Many other substances e.g. alcohols, esters, ketones, sterols, dyes, chlorophyll, proteins etc. have also been found to spread monomolecularly. Thus, Rayleigh's hypothesis of monomolecular spreading originally put forward for the case of olive oil only, now seem to be applicable in general for all the substances stated above.

The study of the nature of spreading of the fatty acid on water surface by estimating the thickness of the spread layer by the area-density method, however, is open to objection. One of the objections against the area-density method, discussed above, is that the density of the layer has invariably been assumed to be equal to that of the substance in bulk. However, this assumption is justified only when the substance in bulk has closed packed layered structure similar to that in the monomolecular film which in general is not true. Therefore, the area-density method can not be expected to yield accurate value of the thickness. However, Langmuir and Adam had great confidence in the area-density method in studying the nature of spreading of fatty acids on water and conclusions drawn by them for the monomolecular spreading are essentially correct, because the density of the monolayer of the fatty acid happens to be very close to that of the acids in bulk.

3.2 SHORT RANGE FORCES AND ADSORPTION: NON-OCCURRENCE OF POLYMOLECULAR FILMS

To provide strong support for the idea of molecular orientation of surfaces and the short range of molecular forces which was developed by Langmuir(164) and Harkins(165) separately, Langmuir performed some classical experiments on adsorption of hydrogen and oxygen in highly evacuated bulbs containing heated tungston filaments. He also believed that the short range forces are responsible for nearly all types of adsorption. Thus, if the surface of a solid or liquid is covered even by a single layer of foreign atoms or molecules, its adsorption properties completely change since the molecules in the consecutive layers can be in contact with those in the preceding one only and not in contact with the substrate.

The concept of short range forces, therefore, leads directly to the monomolecular spreading of the insoluble fatty acids, having hydrophillic (water loving) carboxyl groups in contact with the water surface and the hydrophobic (water hating) methyl groups away from the water in a vertical position. The attachment and orientation of polymolecular chain will not take place in the absence of long range surface forces because the hydrophillic groups in the second layer could not come **into** contact with water. Thus, Langmuir's postulate of short range forces, which is responsible for adsorption on liquid surfaces also can be regarded as the theoretical justification for Rayleigh's idea of monomolecular spreading(152).The occurrence of monomolecular layers of a large number of insoluble substances on water, also give strong support to Langmuir's postulate.

In his work on molecular orientation in surfaces, Hardy(166) believed that the cohesive forces between the molecules to be of long range in nature, often acting through distances of several thousand Angstrom units and thus thought that the orientation extended through many layers of molecules. The observations of Rothen(167) on adsorption involving large molecules, provide definite evidence for the existence of long range molecular forces. Therefore, now it seems that Langmuir's postulate of short-range forces being involved in adsorption phenomena may not be generally applicable and that Hardy's long-range molecular forces do exist in the case of some large molecules.

3.3 FUNDAMENTAL CHARACTERISTICS OF MONOLAYERS

(a) Cause and Mechanism of Spreading of Monolayers on liquids

A nonvolatile substance insoluble in a liquid spreads on its surface if the adhesion (or affinity) between the molecules of the substance and that of the liquid is greater than the cohesion(or affinity) between the molecules of the substance itself(153). The mechanism of the spreading of the substance on liquid surfaces is explained here taking the case of olive oil on water. Water molecules are in constant motion along the surface diffusing long distances and the motion of these surface water molecules cause the expanding movement of the oil drop. Oil molecules adhere to the water molecules and are carried outwards along the surface because of the surface diffusing motions. The surface diffusing motions of water molecules go on continuously underneath the oil drop and the oil molecules which spread first are continuously pushed out farther by the outward surface pressure of those just leaving the oil drop. Obviously, the spreading of a liquid on solid surface can not take place by the above mechanism since the (surface) atoms or molecules of solids remain practically fixed up in their positions.

The spreading and the stability of a foreign monolayer at the liquid-gas interface under given conditions is dependent on a delicate balance among the properties of the substances involved. The substances like long chain fatty acids and alcohols, have a molecular structure composed of a large nonpolar or hydrophobic portion 'the hydrocarbon chain' and at the other extremety a polar or hydrophilic carboxilic or hydroxilic(-COOH or -OH) functional groups. The polar groups tend to confer water solubility, while the nonpolar part prevents it and the formation of an insoluble monolayer is determined by the balance between them. Short chain fatty acids and alcohols such as acetic acid and methyl or ethyl alcohols, are of course, completely miscible with water but the solubility of these substances in water decreases as the length of the hydrocarbon is increased. Thus, in the case of the spreading of stearic acid on water, the adhesion(or affinity) of the stearic acid molecule,containing a polar carboxyl group to the polar water molecule is greater than the cohesion (or affinity) between stearic acid molecules themselves.

Thefore, the stearic acid molecules thus apread out due to the surface diffusing motions of water molecules will attach themselves to the water molecules by their hydrophilic (water loving)carboxyl group (heads) and since the nonpolar hydrocarbon chains with hydrophobic (water hating) methyl group are very weakly attached by water molecules, they remain more or less vertically oriented with the methyl groups (tails) on top. The presence of polar groups in the chain may result in its slight tilting. If the polar or hydrophilic group is not present in the substance, its spreading on water is not possible as is the case with long chain hydrocarbons such as decane($C_{10}H_{22}$) or cetane($C_{16}H_{36}$) and liquid petroleum. These substances do not spread at all, on water. A drop of such oils remains on the water surface as a lens of considerable thickness without spreading. Further, the interactions between and within the molecules forming monolayers are also important. If the intermolecular interactions are strong enough, its spreading as monolayers is difficult even when a suitable polar group is present.

The factors as measured above affecting the spreading depend not only on the nature of the film forming material but also on the nature of both the liquid and gaseous phases. These various factors are also important in governing the structure and stability of an insoluble monomolecular film. To study a certain compound which does not form an insoluble monolayer on pure water, it may be possible to spread it on some other subphase. While the concept of opposing insolubility of a hydrocarbon chain and solubility or water attracting power of a polar functional group is adequate for understanding the formation of monolayers on air-water interface, on the other liquid subphases, other kinds of attraction than the strong dipole-water interaction can be effective. It appears, for example, that n-octacosane, the 28-carbon saturated hydrocarbon, will spread to form a stable monolayer on mercury(168). Presumably, in this case where the liquid subphase has a very high surface tension, dispersion forces are adequate to provide attraction between the organic compound and the surface, and a film is formed in which the molecules are spread out flat on mercury. There are also some fluorinated organic compounds which can spread to form insoluble monolayers on organic liquids. In these cases, parts of the molecules are attracted to the subphase while other parts prevent complete solution.

3.3(b) The Formation of Spread Monolayers

In a conventional manner, the process of spreading of a monolayer with the aid of some volatile solvent, can take place in two ways. Some substances, for example, fatty acids in hexane or petroleum ether on water spreads to form a thin layer whose interference colours are visible. The monolayer forming molecules take up the positions at the solvent water interface and the solvent then evaporates leaving the monolayer on the water surface. In the second method, the drops of the spreading solution do not spontaneously thin out as the case of dilute benzene spreading solutions, but a dilute mixed film of monolayer forming material and solvent is shed from the edges of the droplet, to spread over the available surface. As solvent evaporates from the mixed film, more film spreads from the reservoir of spreading solution droplets. The relative interfacial tensions depend on the nature and concentrations of all the components in the system and in fact change during the spreading process as solvent evaporates. The important aspect of these processes is that at the moment of spreading, the monolayer forming molecules are in environment composed largely of solvent, either as an overlying thin bulk phase or as the diluent in a highly diluted mixed film.

Spreading can also be performed without a solvent in some cases. When a material which does not spread spontaneously, such as a droplet of oleic acid or a small crystal of cetyl alcohol, is placed on a water surface, molecules leave the bulk phase and diffuse out over the liquid, the process of spreading may be hastened by convective flow in the liquid and, in some cases, by vapour phase transport. With sufficient material, the spreading will continue until the surface pressure has risen to the 'equilibrium spreading pressure'. This equilibrium value depends on the relative magnitude of the forces tending to hold the molecules in a monolayer at the air-water interface and those favouring their retention in the bulk droplet or crystal. If the surface available is large enough, the material applied to the surface apread out completely.

3.3(c) States of Monolayers

Henri Devaux(158) shortly after 1900, pointed out that the molecules in the monomolecular films may exist in many different forms corresponding to the three states of matter viz. solid, liquid and gaseous. He showed that the fluidity of a monolayer can be qualitatively estimated from the mobility of talc particles dusted onto the film. Various monolayer states represent different degrees of molecular freedom or order resulting from the intermolecular forces in the film and between film and subphase. The state and stability of the monolayer depends on the amount and distribution of the lateral intermolecular adhesive forces and the strength of anchorage of the molecules to the surface respectively. If the anchorage or the perpendicular attraction between the film molecules and the liquid is weak, the film may not be formed at all or it will tend to crumple up under small lateral compression but if the anchorage or the attraction between the molecules in the monolayer and that of the liquid is sufficiently strong and the lateral adhesion is small the film molecules move about independently on the surface partaking in the translatory motion of the underlying liquid molecules. Such a film resembles a gas or liquid solution on the surface and is called a gaseous or vapour film. A strong lateral adhesion makes the molecules adhere together into large coherent islands of film and restrains their free thermal motions on the surface. The existence of the state of monolayer depends on a delicate balance of intermolecular attractive or repulsive forces. The film is liquid or solid depends on whether the molecular movement is less or more restricted, determined by the amount and small details of distribution of the intermolecular adhesive forces(153).

3.3(d) Fundamental Information About Individual Molecules from Monolayer States

Langmuir's film balance (153) whose range has recently been considerably extended by the use of an electron microscope and radio isotopes (169), remains the principal instrument for basic studies on monomolecular films. With the use of this classically simple device, the primary measurements of the size of the molecules, the estimation of their shape, their cohesion and the location and strength of their charged active groups can be obtained.

The film balance essentially consists of a small shallow waxed trough filled with water on which the monolayer of substance dissolved in a volatile solvent is spread. A barrier in the form of waxed rectangular brass bar is laid across the long edges of the trough behind the monolayer. The film is made to push against a delicately suspended floating barrier which measures the surface pressure exerted by the film as the film is compressed. The pressure of the film against the float is balanced by twisting the torsion wire to which the float is attached. The degree of twisting required to keep the float stationary is a measure of the surface pressure. Greatest care has to be taken to minimise the temperature variation, accidental contamination, vibrations and dust particles, which may cause major errors in the experiment.

A simple curve plotted between surface pressure and area (pressure-area curve of the monolayer) yields, among other things, the cross section and length of the molecule, and the approximate location and strengths of its polar groups. The approximate strength of the intermolecular cohesion or the compressibility of the monolayer can also be obtained by the slope of the pressure-area curve showing decrease in surface area with the increase in surface pressure. Experimentally it is found that the monolayers can be compressed to pressures higher than their equilibrium spreading pressures. It is found impossible to increase the surface pressure further and the area of the film decreases if the pressure is maintained constant or the pressure falls if the film is held at constant area. This condition is referred to as the collapse point of the monolayer. The molecules in the monolayer near the collapse pressure are tightly packed together and the film collapses on slightly increasing the pressure. The cross-sectional area of the molecules can be determined with a prior knowledge of the number of molecules in the monolayer i.e. the number of molecules in the amount of the substance spread. The length of the molecule or the thickness of the monolayer can be found by the area-density method already described(Sec.3.1d). The collapse pressure gives both the strength of anchorage of the film to the surface i.e. the strength of the polar group and the strength of cohesion.

Stearic acid, for example, has been found to have a cross-sectional area of 20 sq.angstroms and a chain length of 25 angstroms. The monolayers of stearic acid have a high collapse pressure of 42 dynes/cm and low compressibility (or high molecular cohesion).

3.4 INHOMOGENEITY OF MONOLAYERS

It was long ago that the investigators assumed the monolayers to be homogeneous at all stages of compression. Zocher and Stiebel(170) by their simple apparatus first examined the monomolecular films to show them to be inhomogeneous at low surface pressure and sometimes even in the region of collapse pressures. His apparatus consisted of a powerful dark field illuminator mounted in the bottom of the trough and focussed on the surface of the liquid bearing monolayer. A microscope was used above the surface to detect inhomogeneity of the film. This technique was later improved by Adam(171), who suggested that varying the liquid level in the trough provided a simple means for accurate focussing. The ultramicroscope has also been used by Braum(172) in an interesting study of collapsed films. The method, however, was capable of detaching only gross impressions of the size and shape of these aggregates.

Later, Freundlich, Bouchet, Tronstad and others have used the elliptically polarized light reflected from surfaces covered by the monolayers, for studying the structure of the films. However, this method could not contribute much regarding the structure of monolayer because of the difficulties in the interpretation of the optical effect of the films in terms of the individual molecules but is capable of indicating the inhomogeneities in the film(173).

Measurements on surface potential, which arises from the surface field of force due to the unbalanced forces of molecules in the surface and therefore varies with molecular concentration or packing in a monolayer, definitely established the inhomogeneity of the films (except gaseous)(174).In this method also, the fine structure of the monolayer could not be resolved because of the dimensions of the electrodes used.

An extensive study of the structures of the monolayers has recently been done by direct electron microscopy by Epstein(175). He showed that it was possible to detect fatty acid monolayer films, after depositing them on glass slides and shadowing with an evaporated metal film. Ries(169) and his coworkers refined this technique to study the monolayer structures at various stages of compression. The electron micrographs taken by them clearly show that at alow pressure the film is inhomogeneous and with increasing compression or pressure large homogeneous areas of continuous monolayer appear. These micrographs also suggested the collapse mechanism and has also been used to determine the thickness of monomolecular films by the shadow casting technique(169). More information about mixed films or monolayers with two or more components was obtained using combined film balance and electron microscope technique in conjunction with radio-active racer technique(169). The results obtained are of biological importance.

The next chapter describes the technique of the building-up of the multilayer films by transferring monolayers on to solids (glass slides). The nature and structural properties of such 'built-up' films and the methods of their thickness determination have also been described. Deposition technique of Y-type films is given in detail as these are used for the present investigations. X-ray and electron diffraction studies are also discussed.

CHAPTER IV

'BUILT-UP' MOLECULAR FILMS AND THEIR PROPERTIES

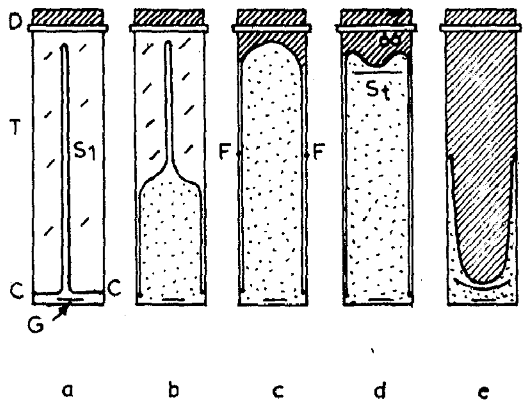
As has been discussed in the preceding chapter, monomolecular films are of great interest because of their formation at surfaces or interfaces. The deposition of multilayers by transferring these monolayers on to the solid surfaces is also equally interesting. The experimental method of 'building-up' of the multilayer films and the nature of such 'built-up' films is described in this chapter. Particularly, the 'building-up' process of Y-type films has been discussed in detail because these films have been used for investigation in the present work. The properties and structure of 'built-up' films as observed by electron diffraction and X-ray diffraction studies have been given here and accurate methods of determining their thickness which is one of the most important aspects for studying the film properties have also been described.

4.1 'BUILDING-UP' OF MULTILAYER FILMS

(a) Experimental

The deposition of mono and multimolecular films of long chain fatty acids can be done by the well known technique of Blodgett and Langmuir(60-62,176). The techique has been described here in detail for the metal stearates, specifically for barium stearate. However, the same method of deposition has been followed for the other substances like barium palmitate, margarate and behenate which have also been studied in the present work.

The technique for 'building-up' of these films, uses a very simple apparatus as illustrated in fig.1. A long narrow trough T heavily waxed from inside is first labelled with the help of the screws provided with it and then the trough is filled with deionized water (specific resistance of the order of $6x10^5$ ohms cm.) to its brim. The surface of water is now cleaned by repeatedly sweeping the barrier across the long edges of the trough and a waxed silk thread is attached by a small clip C to the edges of the trough and the thread is then placed upon the water surface in the form shown in fig.1(a). The thread is carefully made to touch the water surface at every point to avoid any leakage of the film. Stearic acid (or palmitic, margaric, and behenic) dissolved in benzene (concentration almost $3x10^{-4}$ by weight) is placed on the surface near G. This now spreads and pushes the thread before it, as shown in fig.1(b). After the spreading has completed, the thread is fastened to the edges of the trough by two small clips F(fig.1c). A small drop of oleic acid (surface pressure 29 dynes/cm) is now placed on the surface at P to exert a constant pressure on the spread monolayer of the stearic acid. Under these conditions,



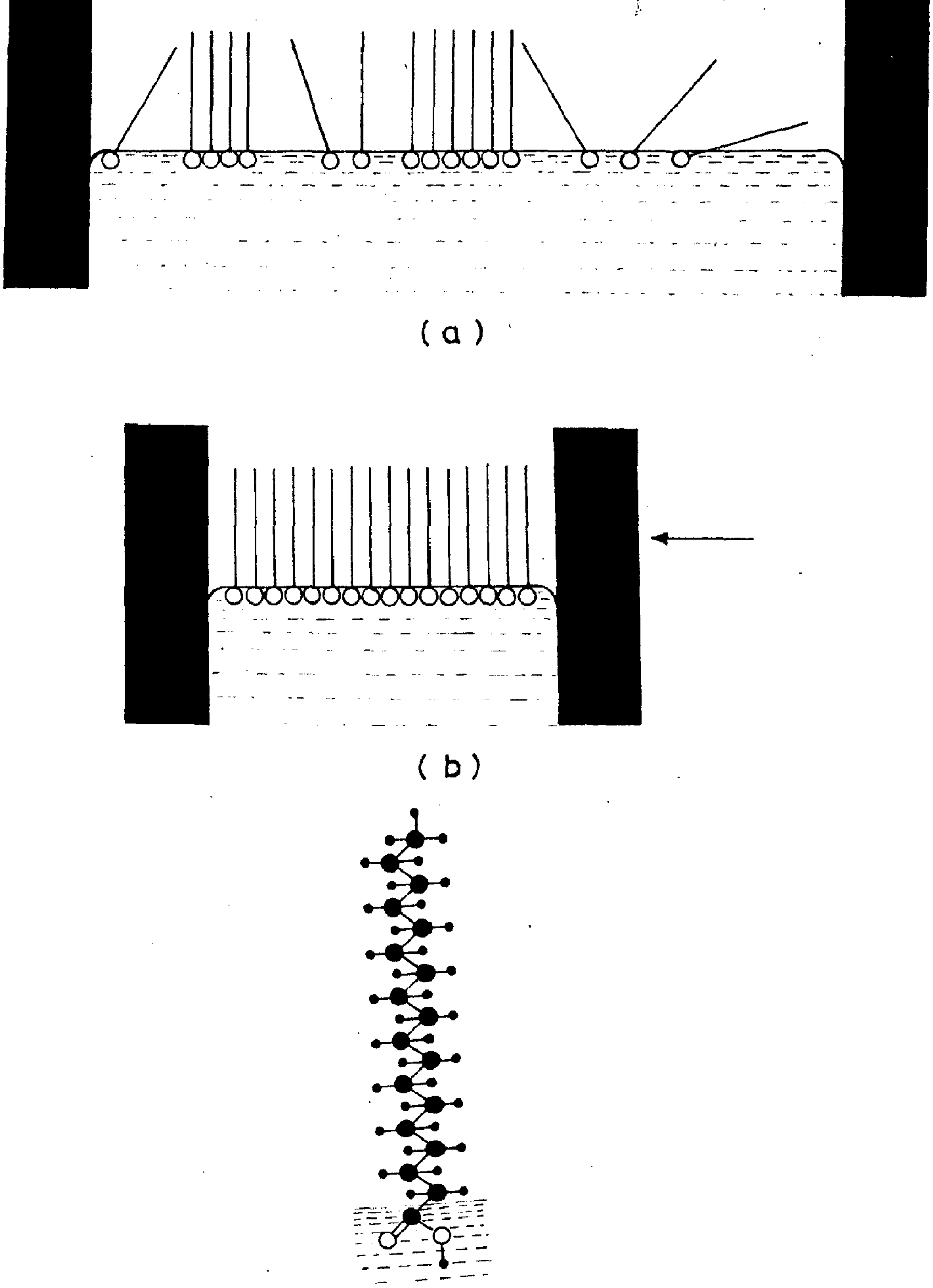
(AFTER LANGMUIR PROC. ROY. SOC. A, 170 1 (1939)

FIG. 1 DIAGRAMMATIC REPRESENTATION OF THE APPARATUS FOR BUILDING UP THE FILMS the monolayer of oleic acid and stearic acid pres against each other and the thread acquires an equilibrium shape as shown in fig.1(d). The stearic acid molecules in the monolayer are now relatively close packed and stand upright as a result of oleic acid compression. The use of the thread S_2 (fig.1(d)) for preventing any accidental oleic acid contamination to stearic acid monolayer near G was not found necessary because it was always ensured that the thread touches the water surface at all points along it and thus, there was no chance of leakage of oleic acid. The deposition by transfer of monolayers upon the solid plate dipped into the water at the position marked 'G' is then started. In successive depositions as some of the stearic acid monolayer is used up, the thread moves forward towards the plate through an area equal to total (front and back) area of the plate.The final shape of the thread, as it gets, is shown in fig.(1e).

For 'building-up' of barium stearate multilayers and the multilayers of other substances most easily, a low concentration (about 3×10^{5} M) of barium ions is added by dissolving 3×10^{-5}M barium chloride in the deionized water. The solution is made alkaline and pH of the solution is adjusted by the addition of potassium bicarbonate to the deionized water already containing $BaCl_2$ in it. The divalent barium ions in the solution undergo surface reaction with stearic acid (or palmitic, margaric and behenic acid) molecules (whose carboxyl groups touch the water surface) to form barium stearate (or palmitate, margarate and behenate). The barium stearate(or palmitate etc.) monolayer is now transferred from the water surface on to the solid, moving across it by a repeatedly dipping and withdrawal process. The ambient temperature during the 'building-up' process should be maintained at about 22°C.

Under these conditions a layer is transferred on both the downward and the upward journey of the slide which is suitably rendered hydrophobic and the built-up film is Y-type. The pH of the solution is held at 7.2 by adding a fixed quantity of potasium bicarbonate ($4x10^{-4}$M). If the solution is made more alkaline (pH=9), the layers are deposited during the down-trips only and not in the up-trips. Such layers are known as X-layers. The layers are preferably deposited at the rate of about 20 to 30 layers per minute.

Before putting the drop of oleic acid on the surface of water the state of the stearic acid molecules which spread monomolecularly on water surface is shown in fig.2(a). Due to relatively large space available for the molecules, some of them may tend to bend over the water surface instead of standing upright. As soon as the oleic acid drop is poured on the water surface, the stearic acid molecules in the monolayer closely packed



(a)

(b)

(c)

(AFTER RIES, SCIENTIFIC AMERICAN, 204, 152 (1961))

FIG. 2 DIAGRAMS SHOWING STEARIC ACID MOLECULES ON WATER SURFACE

(a) MOLECULE BENDING

(b) MOLECULES STANDING CLOSE PACKED

(c) STEARIC ACID MOLECULE STANDING ON WATER

(SMALL SPHERES REPRESENT HYDROGEN ATOMS AND THE BIGGER ONES REPRESENT CARBON ATOMS)

● - CARBON ATOM • - HYDROGEN ATOM O - OXYGEN ATOM together and stand upright as a result of oleic acid compression (fig.2(b)). Figure 2(c) gives a pictorial representation of the orientation of a stearic acid molecule on the water surface with their polar carboxyl groups touching water surface. The circles in the figures represent polar carboxyl groups of the molecules while the nonpolar hydrocarbon chains are represented by the straight lines. It is important to note here that the homogeneity and density of the stearic acid monolayer at this stage would be corresponding to its surface pressure 29 dynes/cm. which is far apart from its colliapse pressure (42 dynes/cm) in the region of the closest molecular packing.

(b) Nature of Deposition of X,Y,Z Types of Films

From aqueous substrates,the experimental possibility of transfering the monolayers onto solid surfaces by a simple dipping and withdrawal process was first realised by Langmuir(177). Miss Blodgett and other subsequent workers(60-62, 176-178) have since carried out detailed investigations of this phenomena, the basic points of which are now well established.Thus, it has been shown that by successive depositions of monolayers, multilayer films with desired number of layers can be 'built-up' on solid surfaces (Sec.4.1(a)).

Only condensed monolayers, which do not tend to spread indefinitely as the surface pressure is reduced to zero i.e. no compression and thus act as two dimensional solids or liquids rather than gases(60) are found to exhibit the phenomenon of deposition on glass or metal surfaces. Initially fatty acids condensed by means of calcium, or barium ions in the substrate were used for investigations (61,62) but subsequently many other types of organic compounds have been employed, e.g. esters, ketones, phenols, proteins etc.

Langmuir(60) and Bickerman (178;179) pointed out that the nature of deposition of monolayers on a solid surface depend on the contact angle between the solid and the film covered water surface. To facilitate the transference of molecules of the monolayer onto the solid surface, the film and the monolayer is supposed to be kept under constant compression during deposition (Sec.4.1a). When a glass or metal slide is being dipped across a fatty acid monlayer on water, for example, the curve of contact between the water and the slide surface advances relative to the slide which gives the 'advancing' contact angle. When the slide is taken out of the water across the monolayer the curve of contact recedes relative to the slide thus giving the 'receding' angle of contact. Obviously, when the slide is entering into the water and the advancing angle is obtuse, the water surface will fold down naturally on the solid surface thus turning the uppermost groups of the monolayer i.e.

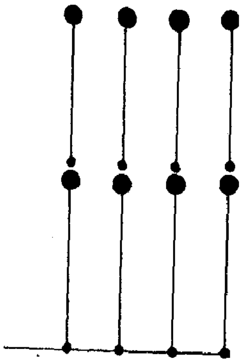


FIG. 3 DIAGRAMMATIC REPRESENTATION SHOWING THE MOLECULAR ORIENTATION IN A X-TYPE FILM

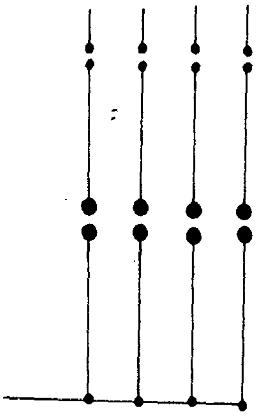


FIG. 3 DIAGRAMMATIC REPRESENTATION SHOWING THE MOLECULAR ORIENTATION IN A Y-TYPE FILM

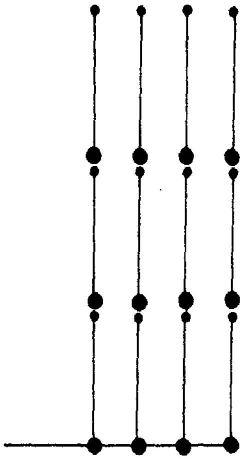


FIG. 3 DIAGRAMMATIC REPRESENTATION SHOWING THE MOLECULAR ORIENTATION IN A Z-TYPE FILM

(IN THE ABOVE DIAGRAMS THE SMALL SPHERES REPRESENT METHYL GROUPS AND THE BIGGER ONES REPRESENT CARBOXYL GROUPS) methyl groups towards the solid surface. The molecules will be deposited with their methyl groups in contact with the slide and the surface of the deposited monolayer will be composed of carboxyl groups (sec.3.1c). This orientation of the monolayer with the methyl groups towards the solid surface and carboxyl groups away from it is termed 'exotropic'. As the adhesion of the methyl groups to the solid surface is relatively low, the slide should obviously be lowered into the water at a slow speed for deposition of the monolayer. The methyl groups in the monolayer remain turned away from the solid surface if the advancing angle is acute and there will be no deposition when the slide is entering the water surface. Thus, a monolayer can be deposited on a slide at its first entry into the water only if the slide surface has been rendered fairly hydrophobic , i.e. non-wettable by water, thus giving a large contact angle. Being easily wettable by water (low contact angle) no deposition of the monolayer therefore takes place on the first immersion of an ordinary glass slide into the water.

When the slide is being taken out and the receding angle is acute the water surface folds up on to the slide thus turning the lower most polar carboxyl group towards the slide surface. The water molecules which are sandwiched between the carboxyl groups of the monolayer and the solid surface are slowly squeezed out because of the strong affinity between the polar carboxyl groups and the solid surface. The polar carboxyl groups in this deposition remain in contact with the solid surface and the surface of the deposited monolayer consists of methyl groups (sec.3.1c). This type of oriented monolayer in which the carboxyl group is attached with the solid surface and the methyl groups away from it is termed 'endotropic'. Evidently, when the receding angle is obtuse the polar carboxyl groups of the molecules in the monolayer remain turned away from the solid surface and there will be no deposition when the slide is taken out from the water surface. Thus,a monolayer can be deposited on a hydrophilic solid surface i.e. easily wettable by water and therefore having a low contact angle, like that of an ordinary glass slide, on its withdrawal across the water surface. In practice it can easily be seen that if the speed of withdrawing the slide is high, the sandwiched molecules will not be efficiently squeezed out and there will be no deposition. The squeezed out water molecules are forced to come down on the surface of water not due to gravity but because of their replacement by fatty acid molecules in the monolayer whose polar carboxyl groups have strong adhesion to the solid surface.

From above it is thus clear that if both the advancing and receding angles are obtuse deposition of the monolayer will take place only on lowering the slide across the water surface. This type of deposition or the film thus 'built-up' is termed X-type. Obviously, the X-type film will be made up of a series of extropic layers which have already been defined to be oriented in such a way that the methyl groups of the molecules are towards the solid surface and carboxyl groups away from it and thus the surface of the X-type film will be composed of carboxyl groups. Since here the molecules in the adjacent layers are oriented in the same direction the distance between the successive planes containing carboxyl groups will clearly be equal to the chain length of the molecule (assuming that the molecules are oriented perpendicularly to the solid surface, fig.3(a)).

When the advancing angle is obtuse and the receding angle is acute the deposition will naturally take place on both lowering and withdrawing the slide across the water surface. This type of deposition or the film thus 'built-up' is called Y-type. A Y-type film, thus, will be made up of a series of alternating exotropic and endotropic layers. Since in the endotropic layer, as has already been defined, the molecules are to be oriented in such a way that the carboxyl groups of the molecules are towards the solid surface and the methyl groups away from it, the surface of a Y-film will be composed of methyl groups. The distance between two successive planes containing carboxyl groups in a Y-type film will clearly be equal to twice the molecular chain length because here the molecules in the adjacent layers are oppositely oriented(fig.3b).

When both the advancing and receding angles are acute the deposition will obviously take place only on withdrawing the slide across the monolayer. This type of deposition, which is rather uncommon or the film thus 'built-up' is termed Z-type. Clearly, a Z-type film be made up of a series of endotropic layers and therefore the surface of a Z-type film will be composed of methyl groups. Since the molecules in the adjacent layers are oriented in the same direction in this type of film, the distance between the successive planes containing carboxyl groups will clearly be equal to the molecular chain length (fig.3c).

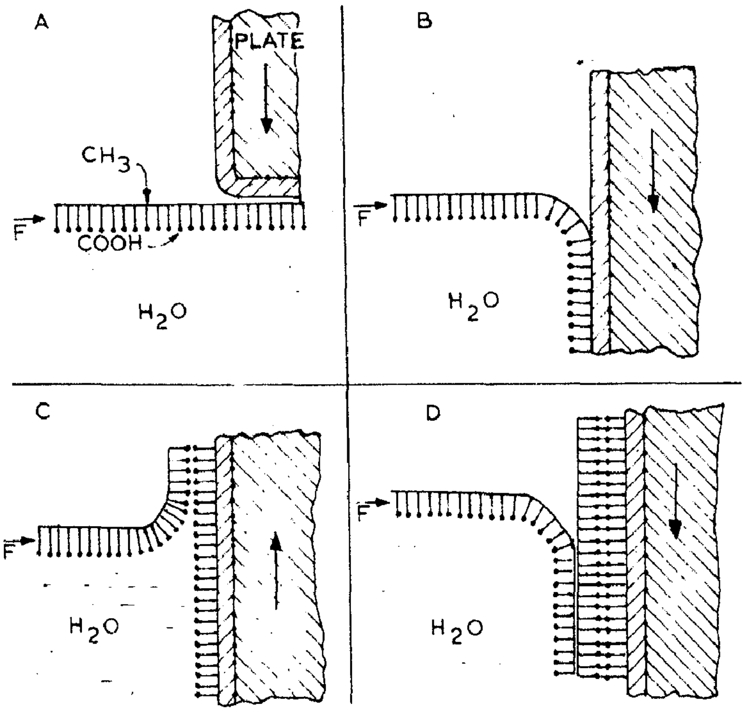
Since the contact angle between the film covered water surface and the solid being dipped is well known to depend on the nature of the film forming substance, the rate of dipping or withdrawal, the surface pressure of the film and the pH value of the water etc., clear cut experimental conditions have to be laid down for the deposition or 'building-up' of any given type of film i.e. X, Y or Z. Blodgett and Langmuir(62) have done this for the case of Y-films of metal stearates.It should also be noted that the contact angle between a liquid and a solid is considerably modified (153) by any contamination, greasy or otherwise,of the solid surface and also by its roughness. Therefore, a great care has to be taken regarding these factors also while performing experiment for 'building-up' a particular type of film.

(c) Deposition Ratio of Monolayer

The early studies of Bikerman(178) who also studied the deposition ratio of monolayers showed that when a close packed film under high surface pressure is transferred to a solid surface, the area of the film deposited is equal to the geometrical area of the solid i.e. the deposition ratio is one. Deposition ratio of a monolayer is defined as the ratio of the apparent area of the slide coated to the area of the monolayer thus removed. Since the surface of a solid is, in general, rough on an atomic scale its apparent area i.e. the one usually measured, is always less than its real area. At the moment of deposition the film bridges over the surface roughness of the solid(178). The deposition ratio of the monolayer was found to be unity within experimental error. This was found to be so even for artificially grooved surfaces and fine wire gauges showing that the deposited monolayer is, in any case initially, stretched over the surface undulations just like a soap film would be.

4.2 THE BUILDING-UP PROCESS OF Y-FILMS

Mono and multimolecular films of long chain compounds (metal stearates) can be 'built-up' by the technique described by Blodgett and Langmuir(61,62). The process for 'building-up' of Y-films by depositing successive monolayers, as have been used in the present work, is illustrated in fig.4. In this case the slide has suitably been rendered hydrophobic by depositing a thin aluminium layer in a high vacuum by thermal evaporation. If the deposition is to be done on glass slide, it is made hydrophobic by placing some molten ferric stearate on the surface and rubbing it vigorously with a clean piece of muslin leaving just one layer of ferric stearate molecules. Figure 4(a) shows the lowering of the slide across the monolayer on the water surface with polar carboxyl groups (as shown by circles) touching the water molecules. Under these conditions, the first layer is transferred on to the slide on the first down trip (fig.4b). The following up-trip causes the deposition of the second layer (fig.4c), the next down journey (fig.4d) gives the third layer and so on. Obviously, the film thus formed on the slide will contain only even number of layers. For getting a film having odd number of layers outside water, the slide is first dipped into the water and then the spreading of the monolayer is done on the surface of water. In this case when the slide is taken out, first layer will be deposited on it. Subsequent deposition made by withdrawing the slide will give the second, third layers and so on. If multilayer film having odd number of layers is to be 'built-up', the previous procedure of



(AFTER LANGMUIR, PROC. ROY. SOC. A, 170, 1 (1939)

FIG. 4 DIAGRAMS SHOWING THE BUILDING-UP PROCESS OF Y-TYPE FILMS dipping and withdrawing of the slide is continued. Obviously, in the deposited Y-film containing even number of layers, both the upper and lower surfaces of the film are made up of hydrophobic methyl groups and in those having odd number of layers, the upper surface consists of methyl groups while the lower one is made up of hydrophilic carboxyl groups.

4.3 EXPERIMENTAL DETAILS AND PRECAUTIONS

In the present investigation extremely pure samples (Price's Bromborough's) of palmitic, margaric, stearic and behenic acids were used. Oleic acid, benzene and wax used were of E Merk's grade. Barium chloride, potassium bicarbonate being of Analar grade. Deionized water was produced by passing the doubly distilled water, through the columns of a portable 'Permutit' deionizer 'mark 8' supplied by M/S Ion Exchange(India) Ltd. . A line diagram of 'Permutit Mark-8' is shown in fig.5. The first column of the deionizer contains the cation exchange material converting cations, such as calcium, magnesium and sodium, into the corresponding acids and the second contains anion exchange material which removes the acids formed by the former. The deionized water thus produced is free from the dissolved salts and other solids and is used for experimentation. The required concentrations of solutions were achieved by weighing the chemicals on an extremely sensitive chemical balance. The pH value

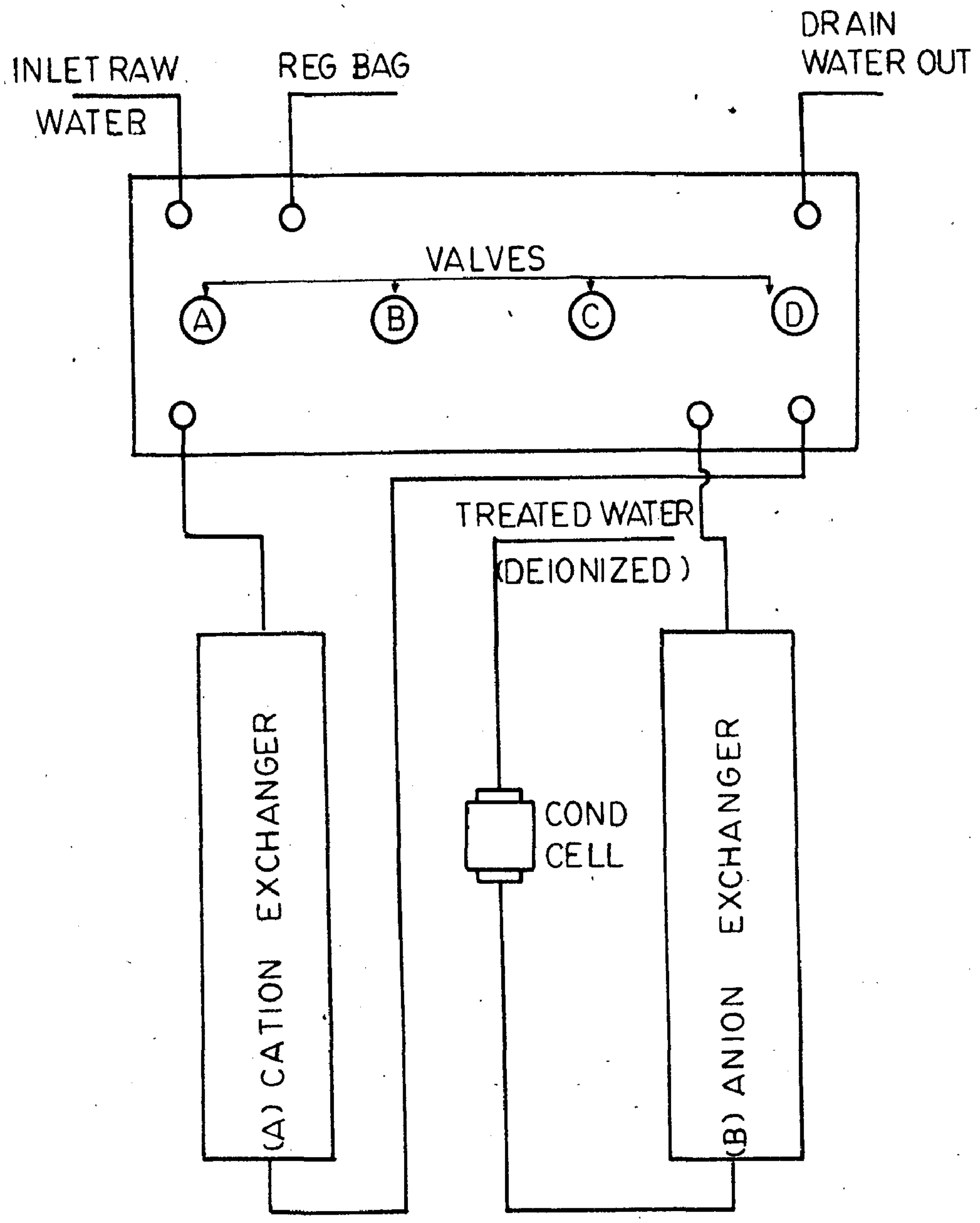


FIG. 5 BLOCK DIAGRAM OF PERMUTIT PORTABLE DE-IONISER MARK [8]

of the solution was checked by the standard Beckmann pH metre. Film deposition is carried out in a room which is air-conditioned and free of dust. Its temperature being maintained to the required value (22^{o}C) with reasonably small variations by cooling it with an air cooler. Greatest care at all stages during deposition was taken against any contamination accidental or otherwise by ensuring and maintaining thorough cleanliness of all parts of the apparatus. This is of great importance as the phenomenon under study being on molecular level and the technique of deposition is delicate. Also, during the experiment much care was taken to avoid any vibration or the disturbance of the trough, which if occurs would crack the spread monolayer and thus produce unevenness in the deposited film. The fabrication of the entire outfit of the apparatus for depositing the films under study was performed by the author himself and a photograph of the same is shown in the labelled fig.6.

4.4 PROPERTIES AND STRUCTURE OF 'BUILT-UP' FILMS

(a) General Properties

The 'built-up' film of barium stearate deposited by the technique of Blodgett and Langmuir, have been studied in detail(60-62,180). The films consist of superposed sheets of oriented molecules and have been shown to form positive uniaxial birefringent crystals, with the optic axis perpendicular to the plane of the film. In the condensed layers of long chain fatty acid soaps, the molecules stand very nearly perpendicular to the plane of the solid surface(181,183). Electron diffraction investigations (182) show that the film actually form hexagonal crystals with the symmetry axis i.e. the optic axis, perpendicular to the plane of the film. X-ray diffraction studies on the films also proved that the films are crystalline in nature forming very thin crystals having known number of molecular layers.

The 'built-up' films of these fatty acid soaps, say, barium stearate can be of X, Y or Z type depending on the molecular orientation in adjacent layers of the films as has already been discussed in Sec.4.1(b). There it has shown theoretically, that the surfaces of Y and Z films should be composed of methyl groups while those of X films should consist of carboxyl groups(in the case of barium stearate, divalent barium ion is substituted for hydrogen atoms of the carboxyl groups). Since the methyl groups are hydrophobic i.e. practically no affinity with water, the surface of Y and Z films are expected to be hydrophobic i.e. nonwettable by water having large contact angle. On the other hand the surface of X-film should be hydrophilic having very low contact angle with water as it consists of hydrophilic (wettable by water) carboxyl groups. However, Langmuir(60) experimentally found that the surfaces of both X and Y films (no work seems to have been done on Z films whose

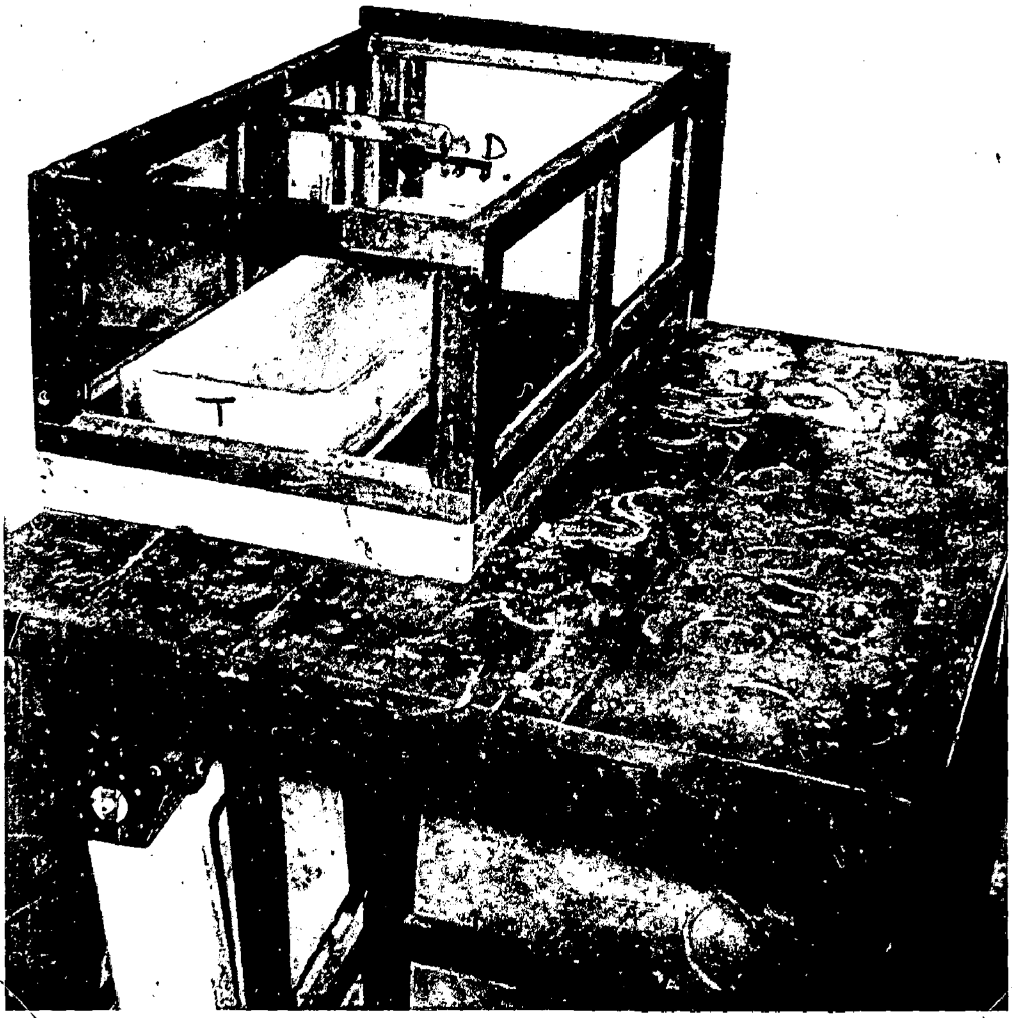


FIG.6- PHOTOGRAPH OF FILM DEPOSITION APPARATUS
T = TROUGH, D = DIPPER

deposition is rather uncommon) have almost the same contact angle with water. Also X-ray diffraction studies of the built-up X and Y-films of barium stearate(184,185) have shown that the lattice spacing normal to the film is the same in both types of films and this spacing is equal to the distance between two successive planes containing barium atoms i.e. carboxyl groups (sec 4.4c). It has already been shown in Sec.4.1b that for X-films the distance between the two successive barium atoms should be half of that for Y-films. The contact angle and spacing anamolies regarding X and Y-films of barium stearate films as described above have been explained by Langmuir (186) in terms of the overturning of molecules in adjacent layers of the X-film, just after deposition. This overturning of molecules in the layers of the X-film which results in a molecular reorientation or a sort of recrystallisation in the film, according to Langmuir arises because of the thermal vibrations. This molecular reorientation can be possible at ordinary room temperatures because the molecules in the films are bound together with very weak Vander Waal's forces as the films have low melting points. The molecules in the first and second layers of a Y film are strongly anchored with their polar carboxyl groups face to face (fig.3b) forming a stable configuration and hence the reorientation of the molecules in these films is not at all expected. This anchoring in the case of X-films is relatively weak due to the methyl(inert) and carboxyl groups being face to face (fig.3a), and unstable configuration. This unstable structural configuration of X-film tends to attain the stable structure of Y-film by the gradual overturning of molecules in the layers of X-films under the influence of thermal vibrations until the molecules in the first and successive double layers of the X-film become strongly and stably anchored with their carboxyl groups face to face. The X-film thus becomes identical to Y film and gives the same contact angle (with water) and normal spacing as the Y-film. However, there is no direct experimental evidence to support Langmuir's idea, his theory of overturning of molecules in X-films accounts for the anamolies as described above.

The surface potential measurements of the X-type films of barium stearate carried out by Porter and Wyman(187,188) show that the films are exotropic in nature and are in the initially unstable structural configuration contrary to the X-ray evidence. Later by his experiments, Langmuir(60) has shown that these surface potentials arise because of some surface electrification produced by the recession of water from the hydrophobic surface during the withdrawal of the slide. However, in the case of Y-films, there is no recession of water taking place.

(b) Studies on Thickness Determination

Mainly two types of methods have been used to determine the thickness of a monomolecular film of a long chain organic substance. Either the thickness was determined by the area-density method (Sec.3.1d) which requires the film to remain on the water surface or by using the well known optical methods which require the films to be deposited on the solid surface. These methods are discussed here in detail.

(i) Area-Density Method

The area-density method for measuring the thickness of monomolecular films on water surface is based on the statement of Dervichian(189) that the lattice structure and tilting of the molecules in different forms are the same in two or three dimensions. The general validity of this theory was, however, questioned by Harkins and Boyd(190) and by Alexander(191). Alexander(157) while working on condensed monolayers has confirmed such criticisms and has shown that the molecular chains in the least compressible region of the monolayer are vertically oriented and are closely packed but not quite as tightly as is possible in the three dimensional crystal. The least compressible region of the monolayer is the one in which it can not be further compressed without making its collapse. The surface pressure of the monolayer in this region is very near to its collapse pressure. Since the built-up films are obtained only with condensed monolayers, the density of the monolayer can not, in general, be assumed to be equal to that of the substance in bulk and as such this method is thus open to objection.

(ii) Optical Methods

(A) Interferometric Method

Blodgett and Langmuir(61,62,180) have determined the thickness of 'built-up' barium stearate films by interference of monochromatic polarized light reflected by the films. In this method the angle of incidence is varied until the reflected intensity becomes minimum. The thickness of the film is calculated from a knowledge of this angle of incidence, wavelength of the monochromatic light used and the ordinary refractive index of the film. Later, Jenkins and Norris(192) also determined the thickness by the same method. In their work they kept the angle of incidence constant and varied the wavelength until the reflected intensity recorded by a spectrophotometer reduced down to minimum. Holley(184) made use of a Michelson Interferometer in another attempt for thickness determination.

(B) Polarimetric Method

To measure the thicknesses very precisely, Rothen and Hanson(193-195) have used an apparatus named 'ellipsometer'. This apparatus is very sensitive and is capable of giving even very small increments in film thickness.

This polarimetric method is based on the measurement of the change in ellipticity of light reflected from the film. The films of stearic acid or barium stearate of known number of layers were used as optical gauge for comparison purposes. Mattuck(196) in a more recent work has used an interference reflector of barium stearate itself to determine the thickness by Hartman's polarimetric method(197) utilising white light interference fringes.

It can easily be seen that these optical methods involved the refractive index of the film and required the use of standard reference films with optical characteristics. These methods give the optical thickness of the film unless an accurate value of the refractive index is used in the calculations for determining the thickness of built-up barium stearate films. As has already been shown that the refractive index of the films can not be assumed to be equal to that of the substance in bulk, hence an unambiguous determination of the refractive index of the films is necessary for evaluating metrical thickness of the films. Also, any differential phase changes upon reflections have to be eliminated to avoid spurious effects in thickness determination.

(C) Multiple Beam Interferometric Method

Tolanksky's multiple beam interferometric technique (198,199) was first used by Courtney - Pratt(200,201) for determining the thickness of molecular films. He applied this method to molecular layers of fatty acids spread by the droplet retraction technique on mica cleavage surface. This method making use of doubly silvered mica, forming the interfernce system, does not directly yield the metrical thickness as it requires the knowledge of the refractive index of the film. Moreover, the differential phase changes upon reflections at mica-silver and monolayer-silver interfaces are involved which are not unambiguously known.

An accurate determination of the metrical thickness of 'built-up' films of barium stearate and other substances have recently been carried out by Srivastava and Verma (202,203) using multiple beam interferometric technique (198,199). Their method is independent of the optical properties of the film and therefore directly determines the metrical thickness. Also, the differential phase changes have been eliminated by using the standard reference film of barium stearate itself, this yields the true metrical thickness of the film.

(c) Lattice Spacing 'c': X-ray Diffraction Studies

The studies of X-ray diffraction on 'built-up' films of various long chain organic compounds have been carried out by many workers (184,185,204-211) making use of the conventional seal-off X-ray source. These X-ray diffraction studies have shown that the 'built-up' films are crystalline in nature and the process of building-up the films is merely mechanically growing the crystal layer by layer. Indeed, the building-up technique can sometimes be used for crystallisation of some otherwise interactable substances, for example, unsaturated acids(209). Most of the workers in their X-ray diffraction studies used relatively thick built-up films having large number of layers while Bisset and Iball(212) investigated barium stearate and palmitate films containing only few layers. They, from their detailed intensified work have established an analogy between optical diffraction from ruled gratings and X-ray diffraction from these layers. Clark and Lappla(213,305) studied a few layers of lead stearate. The lattice spacing of 'built-up' lead stearate films was also measured by Stephens and Turck-lee(214) using electron microscopic technique.

Holley and Bernstein(206,207) and Fankuchen(185) measured the lattice spacing of 'built-up' barium stearate films perpendicular to the plane of the film. The lattice spacing in both X and Y types of films was found to be the same. Since the molecules in the X-films are uni-directionally oriented,their spacing normal to the film should be half to that in Y-films in which the molecules in adjacent layers are oppositely oriented.Langmuir(186) was able to explain the identity in spacings of X and Y films of barium stearate in terms of overturning of molecules in adjacent layers. As the molecules in adjacent layers in a Y-film of barium stearate are oppositely oriented (fig.3b) the barium atoms are located close to parallel planes having a spacing equal to twice the molecular chain length. Since scattering of X-rays from carbon and hydrogen atoms can be assumed to be very small as compared to that from barium atoms (large atomic number), the lattice spacing normal to the film measured by X-ray diffraction must correspond to the distance between adjacent planes containing barium atoms i.e. unit cell height 'c'. Therefore, half of the lattice spacing 'c' must be equal to the chain length of the barium stearate molecule or the metrical thickness of the monomolecular film of barium stearate.

Recently, Srivastava and Verma(203) studied the X-ray diffraction effect in 'built-up' films of barium palmitate, margarate, stearate and behenate and measured the 'c' spacings of these films. A microfocus X-ray source of the kind described by Ehrenberg and Spear(215) was used and the diffracted spectra were recorded on a Bragg-Muller spectrograph. Films were 'built-up' on silvered microscopic slides and it was found that the silver coating of the slide, forming the supporting base for built-up films do not produce any diffraction effects to confuse or interfere with the interpretation of the pattern obtained from the film. The monomolecular spreading of film on water is also supported by the good agreement found between the measured value of thickness by interference and the chain length measured by X-ray diffraction. They also found that the lattice spacing perpendicular to the supporting surface is double the thickness of the monomolecular films.

(d) Electron Diffraction Studies: Determination of Structure

Electron diffraction investigations have been carried out by Germer and Storks(182) to study the structure of mono and multimolecular films of barium stearate and that of stearic acid. They have shown that the 'built-up' Langmuir films of barium stearate, actually form hexagonal crystals with the symmetry axis perpendicular to the plane of the film. The reflection method was used for investigating layers deposited on the clean metal surfaces and the transmission method for those deposited on thin organic supporting foils. It has also been shown that in a 'built-up' multilayer film of stearic acid on a metallic surface the structure of the layer in contact with the surface is identical with the structure of first layer in a built-up film of barium stearate i.e. hexagonal. The structure of the upper layers in the stearic acid acid film is characteristic of the stearic acid itself i.e. monoclinic. This shows that the layer of stearic in contact with the metal surface undergoes chemical reaction to form the metal stearate which has a structure similar to that of barium stearate layer in its 'built-up' film(182). Germer and Storks(182) found that the hydrocarbon chain of barium stearate molecules are separated by 4.85 Å. Recently, Stephens and Turck-lee (214) also used electron diffraction technique for studying the structure of 'built-up' lead stearate films and suggested a monoclinic or orthohombic structure depending on the space group.

Optical studies of barium stearate films have also shown that the multilayers constitute uniaxial crystals with the optic axis perpendicular to the plane of the film. The birefringence is readily demonstrated(62) by placing a 1000 layer film, built on glass, between two crossed nicol prisms or crossed polarised screens. The film being placed at azimuthal angle 45°. The investigation of the birefringence of a 1000 layer film of barium stearate has also been done, later(62) using an ired-gypsum plate in the usual way and the results show that the film behaves as a positive uniaxial crystal. Such uniaxial crystals are characterized by two refractive indices. The refractive indices measured by Blodgett and Langmuir(62) are found to be n_1=1.491 and n_3=1.535 for 'built-up' barium stearate films. The equations used describe the refraction of extraordinary ray, the intensity of the ray reflected from the upper surface and from the film solid boundary, the phase change at the boundaries, Brewster's angle and other properties of birefringent films. Lucy(216) also measured the refractive indices of barium stearate 'built-up' films and found the values, n_1=1.419 and n_3=1.550.

Faucher et al(217) have also developed a theory using Drude's equations for determining the optical constants of 'built-up' barium stearate films on micro-glass slides coated with chromium. Using an incorrect value (48Å) for double layer thickness of barium stearate film, they have shown a good agreement between their theoretical formulae and the experimental measurements. However, the author has shown(218) (reprint attached) that the agreement is not so good with the use of the correct metrical thickness (25.75 Å) for the barium stearate as measured by Srivastava and Verma(202) in their detailed work on these films.

Recently, Tomar and Srivastava(219) have also measured the refractive index of the 'built-up' barium stearate films and other substances by using detector reflectometer consisting of a d.c. differential bridge instead of the usual differential amplifier in the photo-multiplier circuit. Their recent measurements(220) of reflectance and transmittance on such 'built-up' films have tested the validity of Shopper's formulae(221) and have indeed confirmed that these films are anisotropic. A theory of refractive index of the 'built-up' films has also been given by Khanna and Srivastava(222).

The succeeding chapter describes the desirability and advantages of the 'built-up' films which led to their extensive electrical investigations. Method of selection of substrate, cleaning procedure, fabrication details of the experimental set-up are discussed. Sandwich fabrication and measurement techniques of d.c. and a.c. breakdowns have also been described.

CHAPTER V

STUDIES OF DIELECTRIC BREAKDOWN OF "BUILT-UP" MOLECULAR FILMS: EXPERIMENTAL

The capacitor is one of the many circuital components readily fabricated by vacuum deposition and other techniques. Because of ease of deposition, low cost of materials and good temperature stability these components frequently have the construction of metal-dielectric-metal sandwich structure. The dielectric properties of such a device 'built-up' using Langmuir films of long chain organic compounds such as barium stearates etc. have been experimentally investigated by many workers. These 'built-up' molecular films seems to be very promising for making thin film devices in creating insulating barriers, capacitors etc. This chapter gives in detail the information about desirability of these 'built-up' films, fabrication technique of capacitor, the experimental set-up and the method of d.c. and a.c. measurements of dielectric breakdown field.

5.1 DESIRABILITY AND ADVANTAGES OF "BUILT-UP" FILMS

The possible use of thin 'built-up' films in the development of miniaturised solid state devices like field effect transistors, microelectronic and integrated circuitory and other devices, currently enhanced a widespread interest towards their electrical properties, such as, electrical breakdown etc. Particularly, interesting are the dielectric breakdown studies of thin 'built-up' films of barium salts of long chain fatty acids [$CH_3(CH_2)_{n-2}COOH$] of different chain lengths (n is the number of carbon atoms in the chain of fatty acid] such as palmitic (n=16), margaric (n=17), stearic(n=18) and behenic (n=22) acids etc. and the dependence of the breakdown field upon certain conditions such as temperature of the film etc. The study of the variation of the dielectric breakdown field with temperature is important for the theoretical development of the subject and also from the devices point of view as the devices are required to operate at various temperatures. Incidently, the 'built-up' films of barium stearate have recently been proved very promising for making some of the interesting devices(132,136,223,224). Miles and McMahon(223) have shown that barium stearate monolayers may be used as tunneling sandwich between superconductors and their use as dielectric layers has also been shown by Holt(121). These films have been chosen for study because of their highly uniform thickneses which are controllable and have already been very accurately measured by Srivastava and Verma(202,203) using Tolansky's multiple beam interferometric technique. The uniformity of thickness of the 'built-up' film which, obviously, forms an important factor for the present investigations, is achieved by increasing number of monolayers(121) which improves the degree of uniformity. Easy reproducibility of these monolayers and their high structural perfection(225) are the additional advantages of these films.

The films have been **deposited using a delicate** but simple technique of Blodgett and Langmuir, as described earlier in the preceding chapter (Sec.4.2). The films having desired number of layers and hence the films of desired thickness could be built-up by this technique simply by repeated dipping and withdrawal process. The 'fogged' appearance of these films, when the thickness is considerably large (50-500 layers) may be checked by the addition of some copper salt to the solution. The addition of copper ions to the solution also minimise the cracking tendency of the films which increases as the thickness of the film increases, usually commencing at 300-500 layers. However, these problems did not arise in the present investigations as here films of small thicknesses have been used for the study. The monomolecular films of fatty acids thus formed, consist of long hydrocarbon chain perpendicular to the plane of the film with very weak binding forces between continuous chains. These films are structurally well defined consisting of superposed sheets of oriented molecules forming positive uniaxial birefringent crystals with their optic axis perpendicular to the plane of the film(62). These films are crystalline and can be regarded as almost 'two dimensional' crystals.

The 'building-up' of the monomolecular layers.as a special case can be thought to be a layer by layer growth of a crystal. Since the transfer of monomolecular layer from water surface onto the slide requires a high surface pressure, the molecules in the 'built-up' film remain closely packed touching each other. The films thus formed have been reported to be of high structural perfection(225) and to be free from gross defects, porosity and weak spots unlike to that with the evaporated film systems.

It has already been shown by Holt(121) and others that these layers are stable under vacuum and are also thermally stable. Handy and Scala(132) and Mann and Kuhn(134) in their recent studies on these films have shown that it is possible to evaporate metals like aluminium over the deposited films without any damage to the film. This has also been confirmed by the author in his recent studies (226) on the same monomolecular film system. Holt(121) has shown that these films can be heated to in damp air over prolonged periods without damage and observed no change in their electrical properties, even if they are repeatedly and rapidly cycled from liquid nitrogen temperature to 50°C.

As is well known, thickness and temperature are two crucial factors in the measurements of dielectric breakdown strengths, as the former helps in finding the permissible limits of operating voltages and the latter is useful from the point of view of device applications because the devices may be required to operate at various temperatures. While studying the thickness dependent behaviour of dielectric strength, Agarwal and Srivastava (51,52) found that these 'built-up' films have d.c. onset breakdown voltage of the order of several (0-5) volts which has later been confirmed by the author in his temperature dependence studies on the same film system. This leads to their high dielectric strength of the order of megvolts per centimeter (MV/cm). This, therefore, shows that these organic films are highly insulating in behaviour and can be used as good insulators. The microscopic study of the breakdown occured also revealed that these films are free from gross imperfections.

It, therefore, seems desirable that under carefully controlled conditions (sec 4.3) 'built-up' films are eminently suited for such dielectric breakdown studies as have been carried out by the author in the present work.

5.2 SELECTION OF SUBSTRATE AND CLEANING PROCEDURE

Proper selection of the substrate is of major importance because the desired high degree of uniformity of 'built-up' films studied is also governed by the surface structure of the substrate. In the present work, therefore, a considerable attention has been paid to the selection of proper substrates with smooth surfaces, to minimise the appreciable variations in the electrical properties. Primarily because of its smooth surface, chemical inertness, rigidity and ease of cleaning, highly smooth 'Gold-Seal' microglass slides, having no scraches were carefully selected and used. The deposition was preceded onto these substrates, after cleaning them with the procedure as discussed below.

The standard method of matching the cleaned slide surface with a master optical flat (198) was used to see the planeness and smoothness of the slide surface. On proper illumination, the formation of reasonably straight, equidistant, parallel and smooth fringes have shown that he slide is almost plane and its surface has not much urvature. This is, for example, revealed by the absence f 'wriggle' in the fringes of equal chromatic order, aken by Srivastava and Verma (202,203) on a four-layer barium stearate film(thickness about 100 Å). After performing such extensive investigations, it was found that the 'Gold-Seal' micro-glass slides, in general do not have sharp projections and waviness.

The micro glass slides after selecting by the above discussed procedures are, first of all, physically cleaned by soap solution in deionized water and subsequently rubbed and rinsed with carbon tetra chloride to remove any dirt and visible fringe prints. After washing with carbon tetra chloride, these slides are stored in

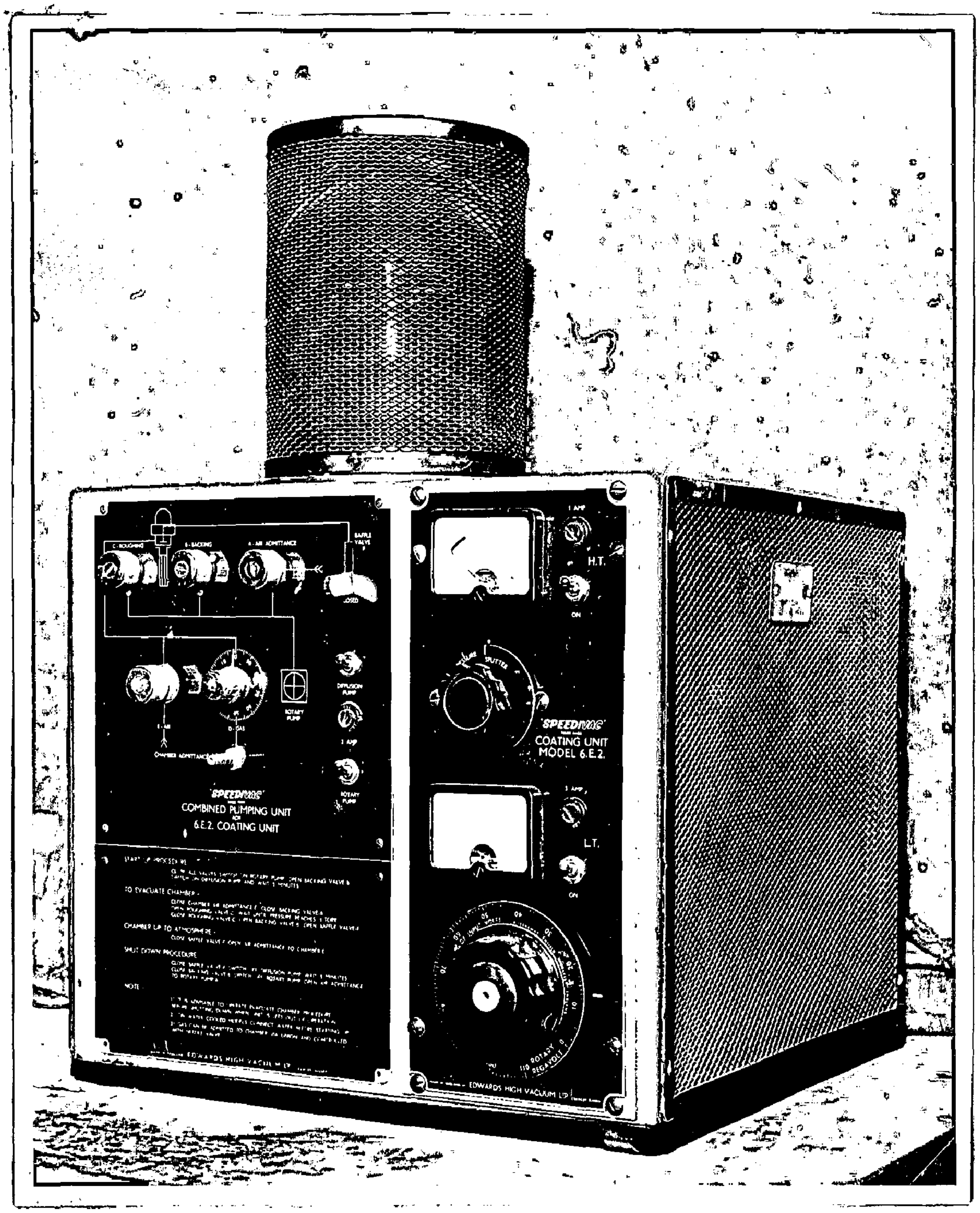


FIG.7- PHOTOGRAPH OF COATING UNIT
MODEL 'SPEEDIVAC 6E2'

warmed and freshly prepared chromic acid (35 c.c. of potassium chromate and 100 c.c concentrated sulfuric acid, both of highly pure quality) for about one hour, which is the most effective cleaning agent. These slides are now washed with deionized water and boiling it in water for about ten minutes. After washing it in deionized water and soaking in freshly laundered old linen, it is rubbed vigorously and smoothly with clean dry cotton wool until no 'breath figures' are obtained by heavily breathing on it. These thoroughly cleaned glass slides are now ready for sandwich fabrication as will be discussed later(Sec.5.3). To remove the metal electrodes (aluminium films) from the old used slides concentrated nitric acid is used and then the slides are prepared for use by the above said procedure. These cleaned slides were preserved in a thoroughly cleaned glass container till these were loaded in the vacuum chamber.

5.3 FABRICATION OF FILM CAPACITOR

The desired shaping of thin film involves any or all deposition and masking techniques in a variety of sequences. For the sake of simplicity physical masking technique is used in which the mask is mounted between the evaporant source and the substrate in contact with the latter. The cleaned and carefully selected microglass slides as discussed in the preceding section are used for fabricating the film sandwiches of the type

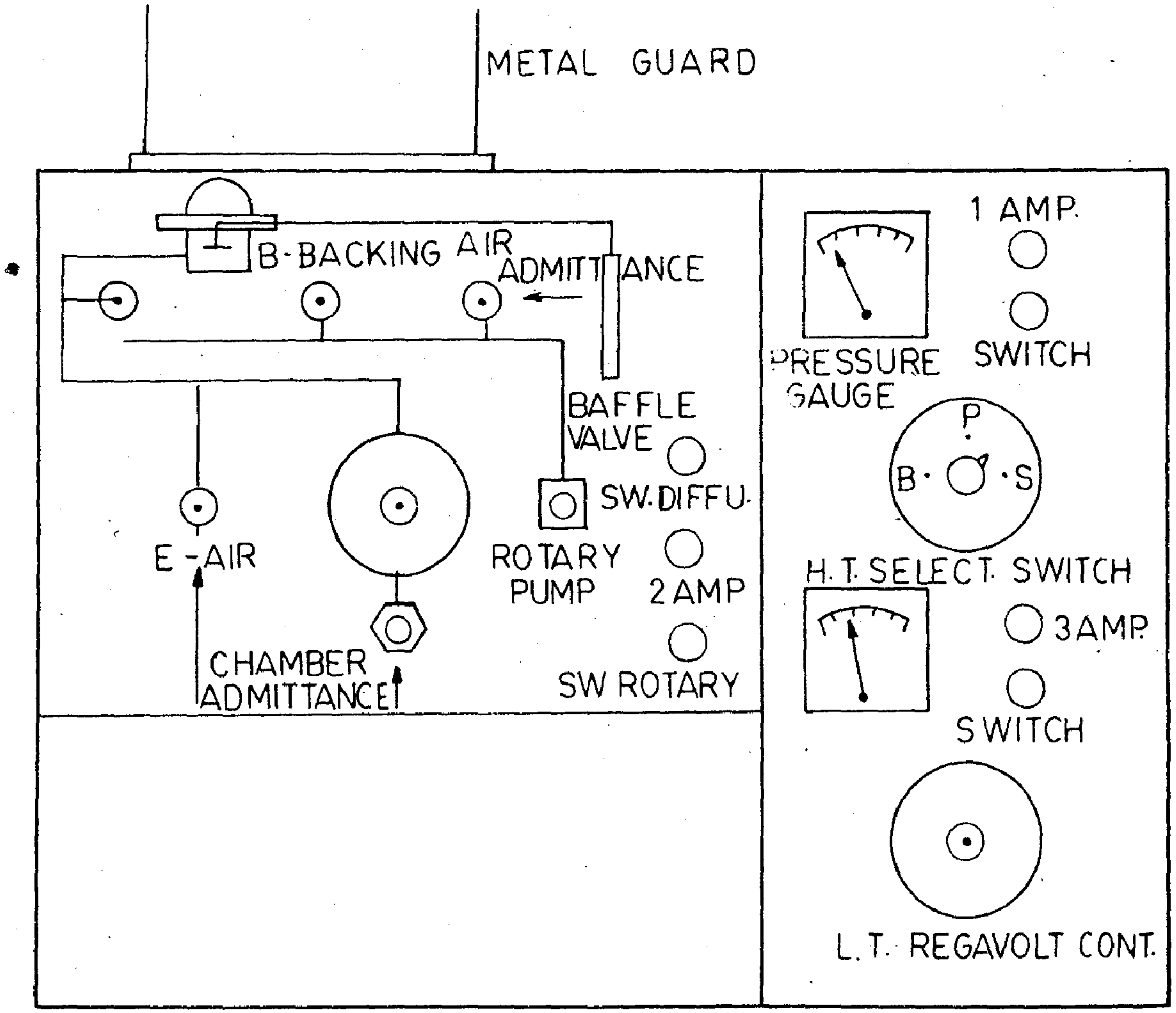


FIG.8 BLOCK DIAGRAM OF SPEEDIVAC MODEL 6 E2 VACCUM COATING UNIT.

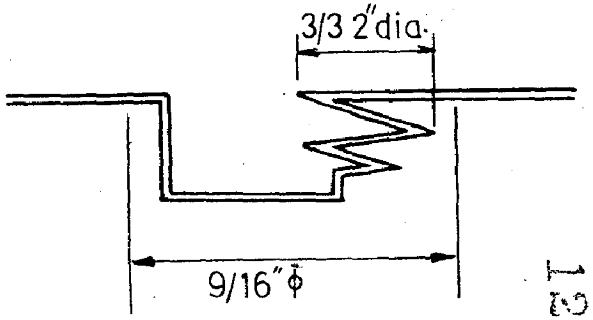


FIG. 9 TUNGSTEN BASKET.

Al-Film-Al. For obtaining the required sandwich structure, about two-third part of the slide was first aluminized by using a flat mask which is made of a thin copper foil of 0.125 cm thickness (about 2 cms. long and 1 cm. broad in dimensions). The aluminium was deposited on the slide by thermal evaporation in vacuum ($\approx 10^{-6}$ Torr) with the help of Edward's 'speedivac' model 6E2 coating unit (fig. 7) which provides safe and easy evaporation facilities in a compact unit. This unit is equipped for evaporation, sputtering and ionic bombardment. It consists of a four inch silicon oil diffusion pump with a water cooled baffle backed by a mechanical pump. Generally, two hours are required to pump the system down to about 10^{-6} Torr. The deposition chamber is a pyrax glass bell-jar which rests on finely grinded surface with a rubber 'O' ring. The diameter of bell-jar was 6 inches at the base. Inside this bell-jar the work holder is fitted above tungsten filament. The distance between the filament and the work holder surface at which the slides were placed was always kept fixed equal to 4 inches. A line diagram of the evaporation set-up is also shown in fig.8. Tungsten baskets of the type H140/121, as shown in fig.9, have been used for evaporation of aluminium which were supplied by M/S Edwards High Vacuum Ltd., Sussex, England.

After proper mounting of filament and slide holder in the work chamber, it is sealed and evacuated by operating the unit in subsequent steps. The high tension

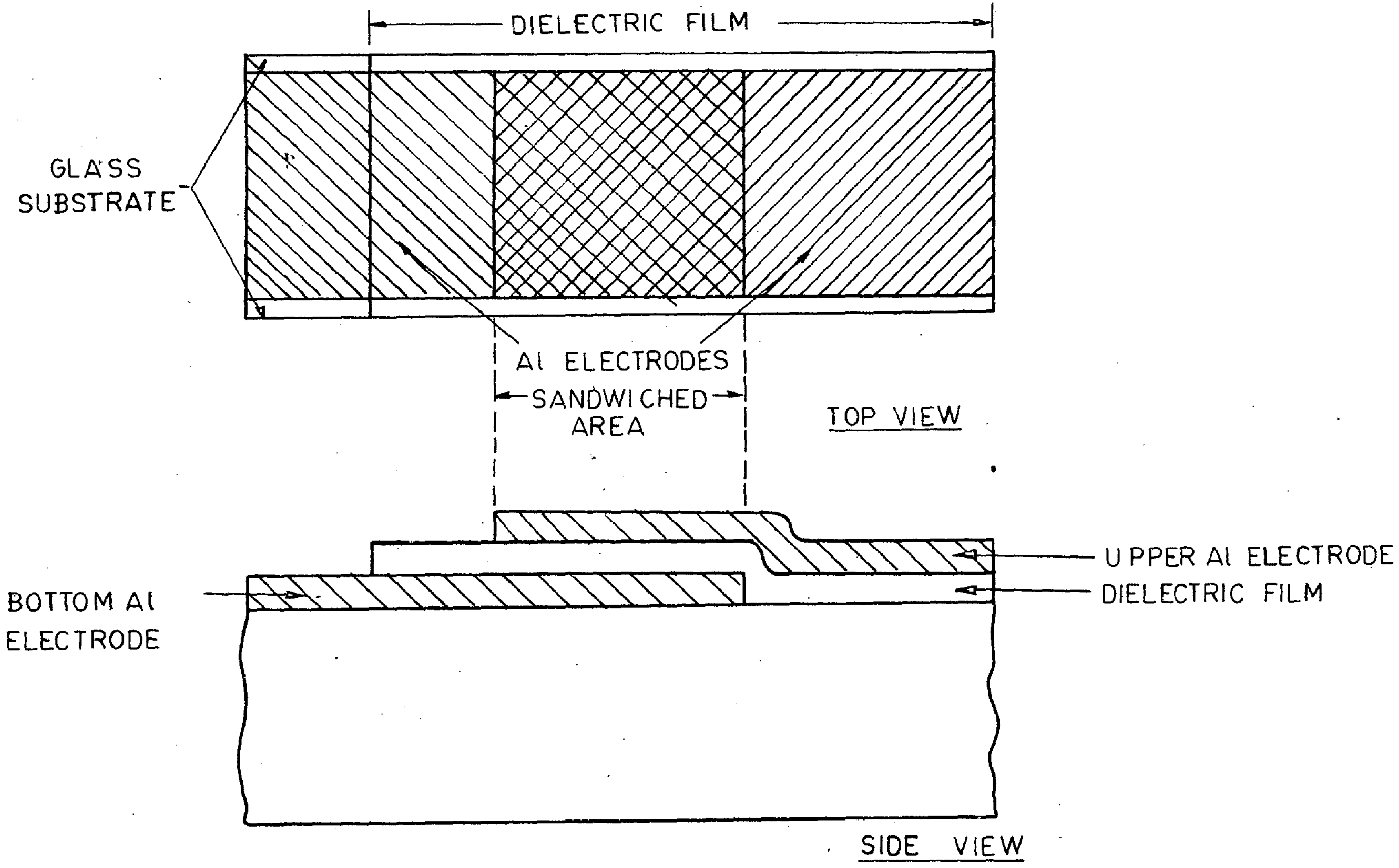


FIG. 10 SKETCH OF THE FILM SANDWICH SYSTEM (Al - FILM - Al)

bombardment current is switched on to clean the chamber interior and work surface (slide). After the evacuation process is completed and the pressure gauge indicates a required pressure of the order of 10^{-6} Torr, the low tension current to the evaporation source is switched on and increased by means of a 'regovolt' control unit very slowly till the aluminium piece placed gets evaporated.

99.9% pure aluminium wire supplied by M/S Johnson and Mathey was used for evaporation and making electrodes of the sandwich structure.The thickness of the aluminium electrode was roughly kept constant every time by keeping the distance between the filament and the work holder fixed and placing the same amount of aluminium and the same low tension current is passed for a fixed time, for its evaporation. Anhydrous phosphorous pentaoxide of Analar grade was used every time when the evacuation is done and high vacuum is created in the bell-jar to remove any moisture in the work chamber. By controlling all these factors, thin aluminium (Al) electrodes were evaporated each time.

The built-up films of barium salts of long chain fatty acids of different chain lengths like palmitic, margaric, stearic and behenic are then deposited on these partly aluminized glass slides having desired number of layers by using the Blodgett-Langmuir technique as discussed earlier (Chapter 4 Sec.4.1a). Y-type films have been used for study because their characteristics are well understood. In this deposition, the slide into the water is dipped keeping aluminized portion of the side upward and the film is deposited on about 2/3rd part of the slide. The upper Al electrode is then evaporated on the film repeating the above discussed procedure when the film is dried-up. The upper electrode is deposited in such a way that sandwich structure of the type Al-film-Al is obtained. The lateral and transverse views of the sandwich structure thus fabricated is shown in fig.10. During the evaporation of upper Al electrode, ionic bombardment cleaning is avoided which causes local heating of film, resulting into the melting of the organic films having molecules bound together by weak Vander **Wall forces**.It has already been established that the thermal evaporation in vacuum does not cause any damage to the deposited film(121). The film sandwiches of the area approximately equal to 0.4 cm^2 are now obtained which are ready to use for electrical breakdown measurements. The area of the film capacitors were measured using a travelling microscope.

5.4 FABRICATION OF THERMAL PROBE,CRYOSTATIC ARRANGEMENT AND EXPERIMENTAL SET-UP

Determination of the strength of the materials at cryogenic temperatures is virtually important to permit the efficient and safe design of cryogenic equipment, since low temperatures have marked effects on the properties

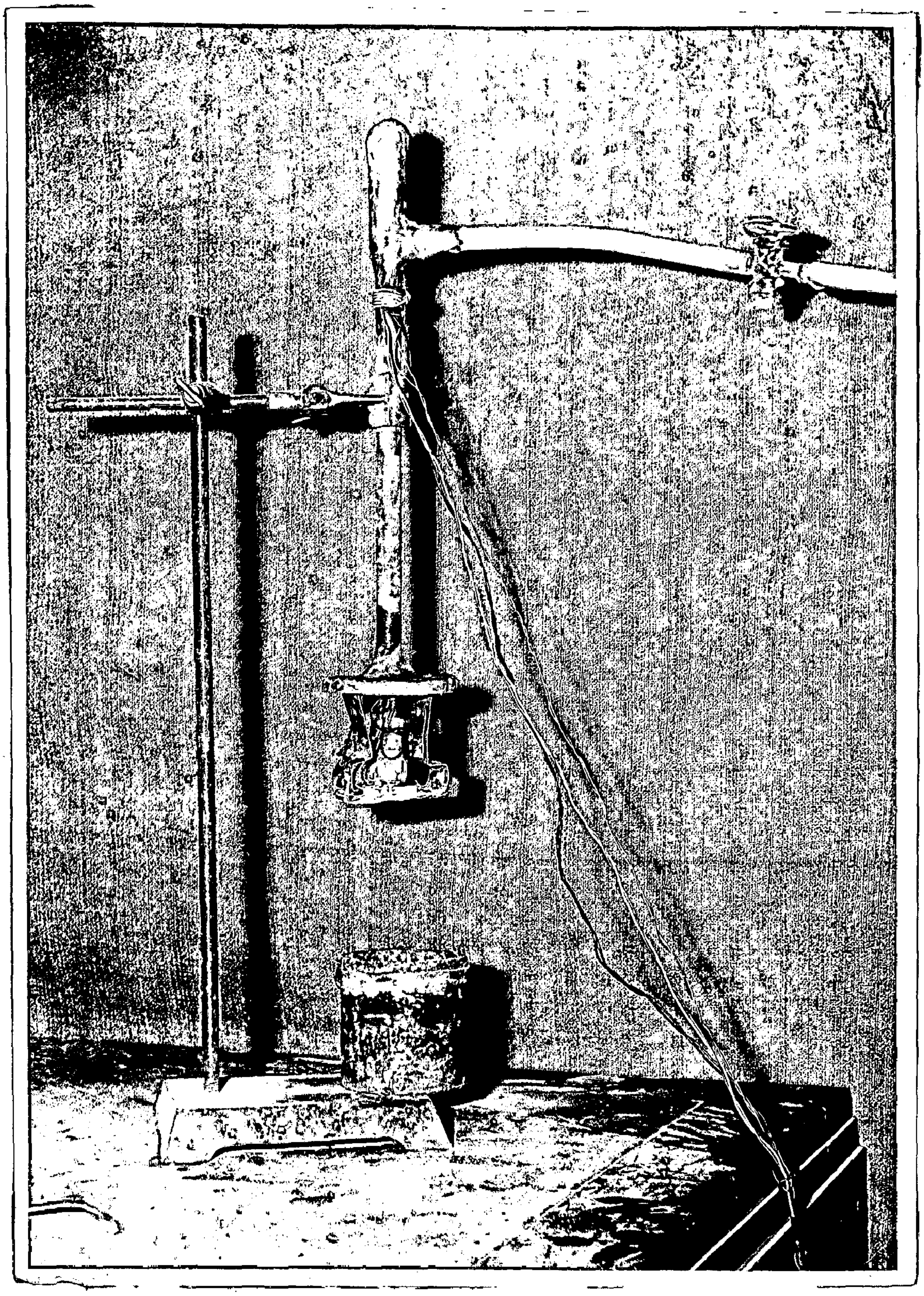


FIG.11- PHOTOGRAPH OF THERMAL PROBE

of many materials. For variable temperature measurements of the electrical breakdown characteristics of the 'built-up' thin films, a suitable cryostatic arrangement was designed and fabricated by the author. The arrangement consists of a thermal probe (a photograph of the thermal probe is shown in fig.11) and a heat shielded, white painted wooden box, well insulated from the surroundings to minimise the heat loss. It also consists a finely silver polished Dewar flask.

The thermal probe was a big copper rod(12" long and 3/4"diameter) whose one end was sealed after passing connecting leads through it. The ceiling was made using a low melting point solder known as 'woods-metal' (Bismuth 50%, lead 25%, tin 12.5% and cadmium 12.5%). This is used with $ZnCl_2$ as flux. Over this a coating of araldite (a high power adhesive) is done to become sure of its being air tight. An opening is also made in the copper rod to which the high speed rotary vacuum oil pump 'Lectrum' (Apee Electricals, India) was connected with a rubber tube having a two way glass valve in between the pump and the rod for the purpose of creating vacuum or passing air into the probe system as desired. At the other end of the metal rod a copper capsule (3"diameter and 3"long) was welded. This is facilitated by a lid which can be opened and can also be sealed-off with the help of 'woods-metal' and 'plasticine'. The capsule consists of a copper support (test specimen holder) which is fitted tightly with the

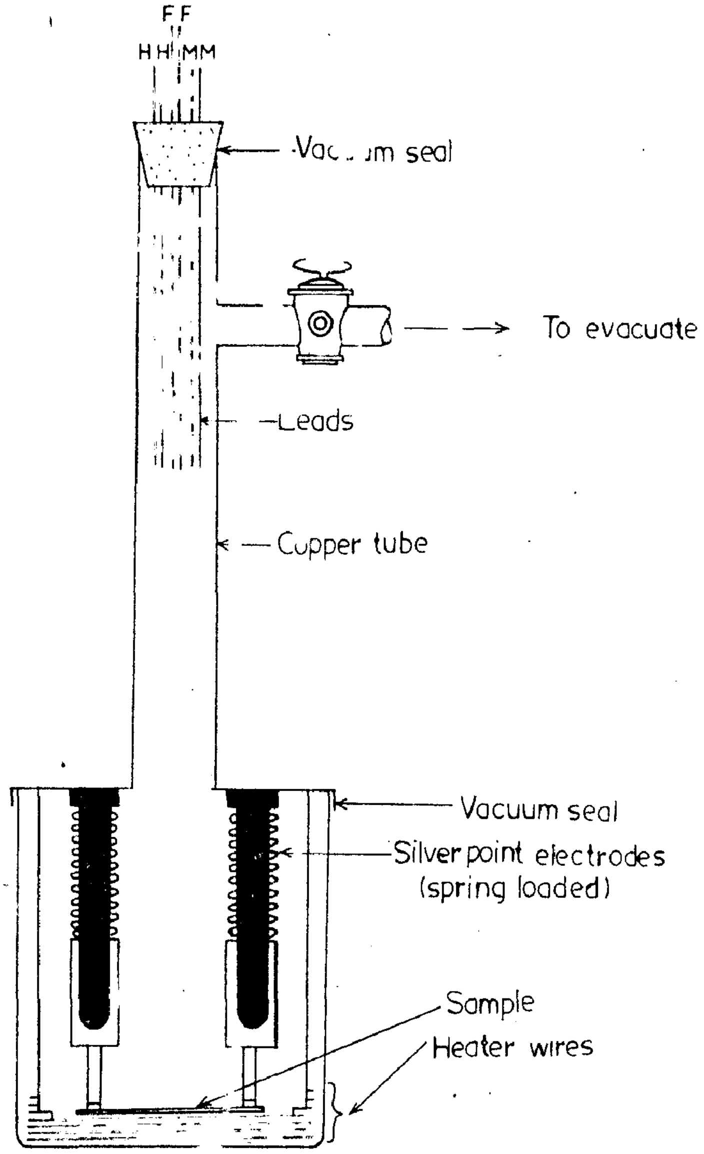


FIG.12 - Design of probe for studying the break down in thin films at different temperatures.

lid of the capsule. Over this metal plate, two springloaded silver point contacts were made to rest which are externally connected with the measuring circuit and in the capsule the test specimen is placed below these silver point contacts. The special advantage with this type of arrangement is that the film always is under same constant pressure touching the cooled surface very tightly. The spring loaded system make proper contacts of the lead with the test sample and the possibility of disrupting the film at the place of contact is reduced to minimum.

Thermocouple device in which a pair of dissimilar metals (e.g. copper-constantan) generates a voltage at a junction being easier to build and to read have been used for measuring the temperature of the test specimen when placed in the metal capsule in conjunction with a highly sensitive d.c. microvoltmeter system having a sensitivity of 1 microvolt per division. Calibration curve of the thermocouple system is given in fig.12B. The calibration curve was obtained through the courtesy of Low Temperature Division, National Physical Laboratory, New Delhi, India.

The specimen holder is fitted with a terminal of the thermocouple used through a small piece of same microglass slide onto which the test samples are fabricated and the heater wires, all forming a compact structure (the line diagram of the test sample is given in fig.10). The other end of the thermocouple system is used as a reference

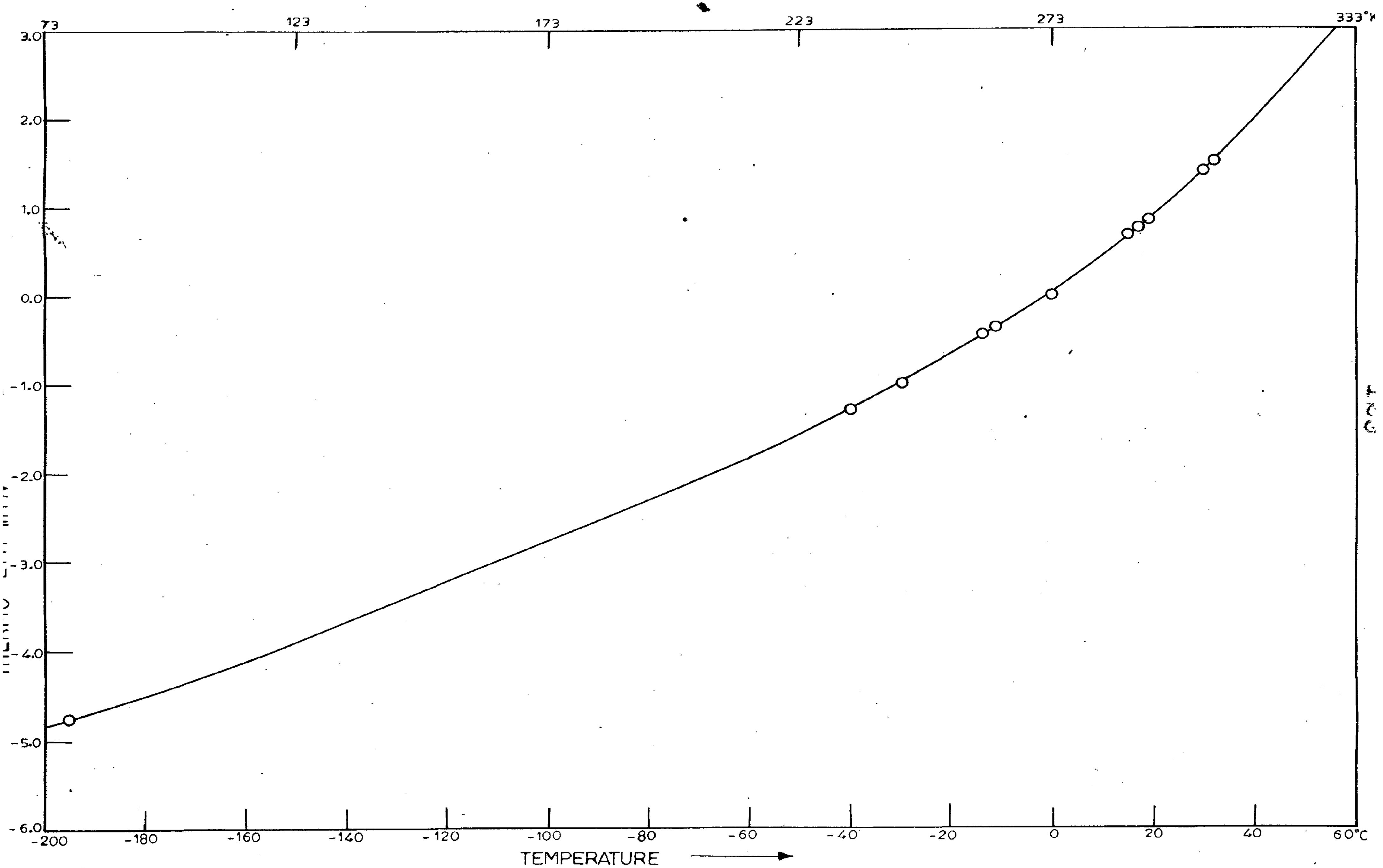


FIG.12B_Temperature v/s Thermo E M F curve for copper-constantan thermo couple system.

junction and is kept always in an ice bath (i.e. at 0°C). The heater wires are connected with a variak (variable output power transformer) to produce the required heating of the specimen which after sometime acquires steady temperature. The temperature of the film sample is then read with the help of a sensitive 'Phillips' d.c. microvoltmeter. To remove the moisture from the capsule, highly anhydrous 'Analar Mark' phosphorous penta oxide was used as drying agent.

The test sample is placed on the slide holder under spring loaded pressure leads and the contacts were made through mercury drops. Direct contact of the aluminium electrodes with the leads was avoided because of the possibility of disrupting the film from the place of contact. After putting a small quantity of fresh phosphorous pentaoxide (P_2O_5) inside the capsule, it is sealed very properly to make it air tight from all the sides with the help of wood's-metal and plasticine and then it is evacuated with the help of a motor. This probe is now placed very gently inside a Dewar flask which is a double walled vessel with a high vacuum between the walls and very finely silvered from in and outside. This is enclosed in a heat shield of very thick sheets of thermocole whose thermal conductivity is as low as 0.02 cals/°C. The whole system is placed in a white painted wooden box containing cotton wool all around it to further insulate the system from the surroundings.

The capsule is cooled with the liquid nitrogen and its temperature could be varied between 77°K and 320°K. A photographic representation of the whole set-up is given in fig.13.

5.5 ELECTRICAL BREAKDOWN MEASUREMENTS

For testing the fabricated capacitors, first of all the resistance of the samples is checked with the help of a sensitive 'Philips' multimeter and only those samples were selected for breakdown tests which showed a high resistance. The testing of the sample is done at very low voltages (0.1 volts). The d.c. breakdown measurements on the 'built-up' molecular film sandwiches were made using silver probes through mercury droplets to contact the aluminium electrodes at both the ends of the sandwich. After the sample to be tested has acquired the required temperature and steady state has been reached, electrical stresses are applied to the sample with the help of appropriate electrical circuits designed and fabricated by the author himself.

(a) Direct Current Measurements

The d.c. measurements of the breakdown voltages and the current-voltage characteristics were carried out using a 90 volts 'Eveready' mark battery across the sample with and without a series resistor ($\simeq$ 4.7 K) between the source and the sample. The voltage is swept-up from its

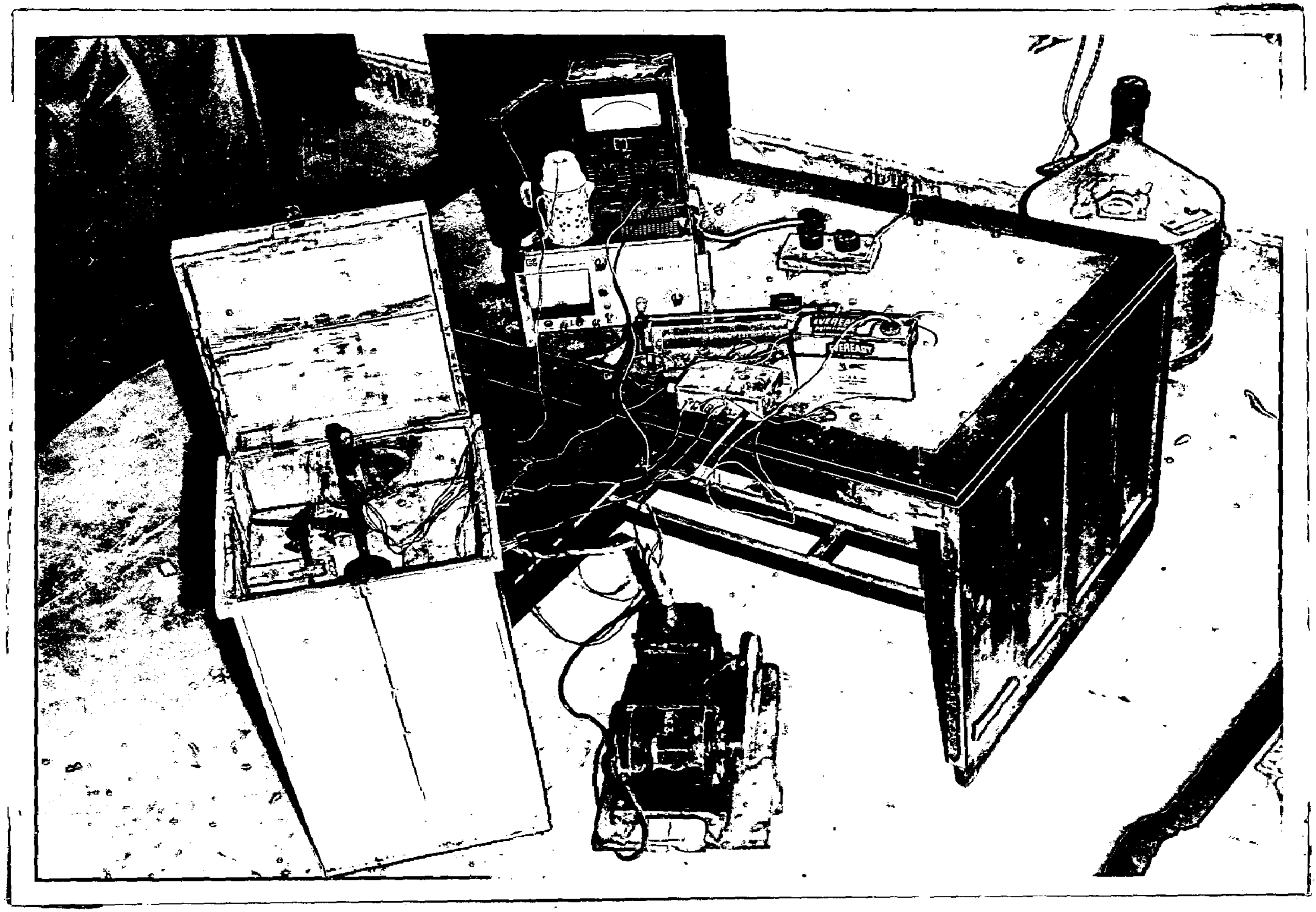
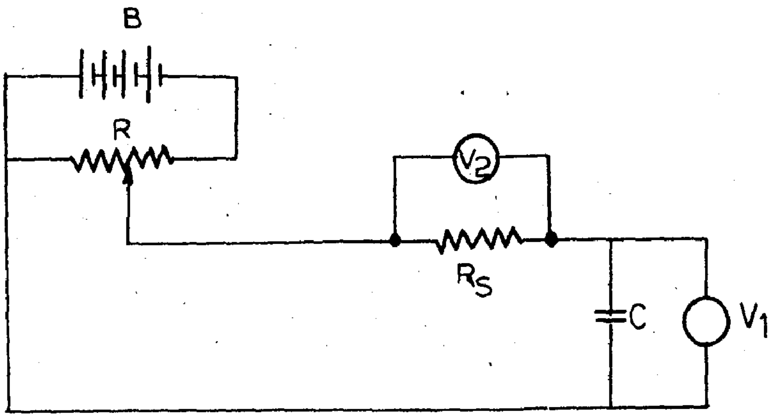


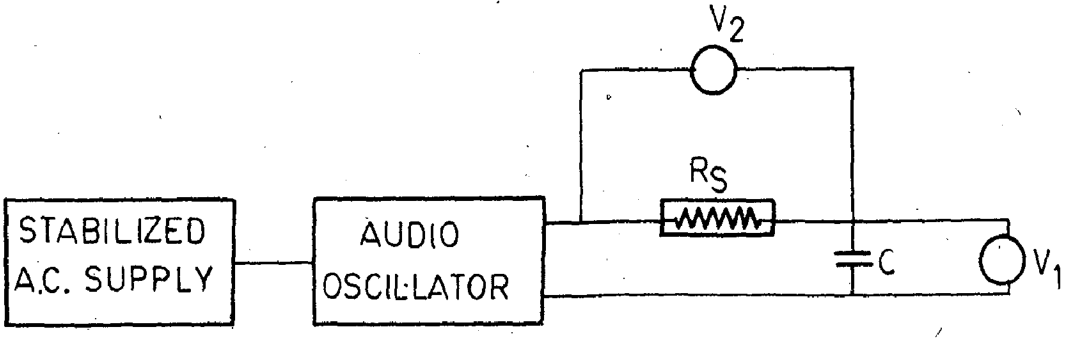
FIG.13- PHOTOGRAPH OF THE MEASUREMENT SET-UP

low values by feeding it through a linear wire wound potentiometer 'helipot' ($\simeq$ 100K) and the sample is, thus, exposed to linearly rising voltage. The breakdown voltage (V_b) corresponding to the onset of breakdown, shown by an abrupt rise of current, the destructive breakdown voltage (V_{db}) at which a large area of the film capacitor gets destroyed and the current ceased to flow in the circuit, were measured with a precision V.T.V.M. having a sensitivity of 0.02 volts per division. The current was recorded in the nondestructive phase (starting from onset breakdown voltage) using a sensitive 'Philips' ampere meter (sensitivity 0.5 microamperes per division).The circuit diagram is shown in fig.14. The destructive breakdown events were accompanied by the sparks produced across the capacitor. The destruction of the film was observed under a microscope 'Carl Zeiss Jena(Germany)' with a camera attachment and magnified photomicrographs of the film destruction were taken using this camera attachment in transmission. The photomicrographs were also taken using reflection technique with a projection microscope 'Neophot-2(Germany)' with a plate camera attachment with it. 'Scientia' films supplied by 'Agfa-Gavaert' were used and an exposure of about 5 minutes was allowed every time when transmission photographs were taken while an exposure of 1 minute was given while working with the reflection microscope.



V_1 - V T V M, V_2 - ELECTRONIC MULTIMETER, R_S - STANDARD SERIES RESISTOR, R - HELIPOT, C - FILM CAPACITOR UNDER TEST.

FIG.14 CIRCUIT DIAGRAM FOR D.C. MEASUREMENTS



V_1 - V T V M, V_2 - ELECTRONIC MULTIMETER, R_S - STANDARD SERIES RESISTOR, C - FILM CAPACITOR UNDER TEST.

FIG.15 BLOCK DIAGRAM FOR A.C. MEASUREMENTS

The measurements of the breakdown voltage have also been taken by changing the polarity of the bottom and top aluminium electrodes of the symmetrical structure, Al-Film-Al, presently investigated. The breakdown voltage in both the cases is found to be the same. It is thus concluded that the oxide layer which is formed on the upper surface of the bottom electrode of aluminium (due to its exposition into the air) does not play any role in the conduction mechanism of these organic monomolecular layers. These observations have been supported by Mann and Kuhn(134) who have measured the conductivity of these monomolecular multilayer system with and without taking account of oxide layer and have shown that the conductivity remains same even when the aluminium electrode is annealed in air at 300°C.

(b) a.c. Breakdown Measurements

A low distortion audio oscillator (Philips) was used to measure the a.c. breakdown voltages. This has been used in conjunction with a stabilized power source and the resultant output voltage of the a.c. source, swept-up from its low values, was applied across the sample having a standard series resistor ($\sim$10 K). On linearly increasing the voltage, an anormous rise in the current at fixed voltage was observed which is known to be the 'a.c.onset breakdown voltage'. The voltages are again recorded by a precision V.T.V.M. having sensitivity 0.02 volts per division. The circuit diagram is shown in fig.15.

The next chapter describes the results of detailed and systematic temperature dependence study of d.c. breakdown characteristics of the 'built-up' Langmuir films. The results have also been discussed and an attempt is made to interpret in terms of the existing theories.

CHAPTER-VI

RESULTS ON D.C. BREAKDOWN AND DISCUSSION

This chapter describes the results of detailed and systematic measurements on d.c. breakdown strength taken on 'built-up' Langmuir films of barium palmitate, margarate, stearate and behenate using the procedure discussed earlier in the last chapter. Two types of breakdown events widely different from each other were observed, one for the 'onset' of breakdown at which the current through the insulator shoots-up suddenly from its low values and the other 'maximum breakdown voltage' at which a large area of the insulating film gets destroyed and is also termed as 'destructive breakdown voltage'. The results concerning the temperature dependence studies of these two breakdown events are described and discussed here.

6.1 RESULTS

(a) Temperature Dependence of Breakdown Field

The d.c. 'onset' breakdown studies have been carried out for the films of barium palmitate, margarate, stearate and behenate $[CH_3(CH_2)_{n-2}COO]_2Ba$, with different chain lengths 'n' (n gives the number of carbon atoms in the hydrocarbon chain). The measurements of the temperature dependence of this breakdown voltage and hence the breakdown field have been taken over a range of temperatures varying from about 77°K to 320°K (liquid nitrogen temperature to room temperature) with different number of layers i.e. with different thicknesses both at moderate film thicknesses (20 layers) and also in the ultrathin range (1-10 layers). Graphical representation of the temperature dependence of the d.c. 'onset' breakdown field (F_b)(the field is obtained by dividing the breakdown voltage observed with the thickness of the film in cms.) in 'built-up' barium palmitate films (n=16) has been shown in fig.16. Plots A, B, C and D are the 'best-fit' experimental curves for 2,4,8 and 20 layers thick barium palmitate films.The curves A', B', C' and D' also plotted on the same figure and shown with dotted lines give the calculated breakdown field for 2,4,8 and 20 layers barium palmitate if the injection of electrons is governed purely by the Schottky emission(44). These curves have been shown for purposes of later comparison with theory and to interpret the results obtained here. The theoretical curves corresponding to the tunnel emission have not been given because the temperature independence of the breakdown field is implicit in the Forlani-Minnaja theory(44). In this electron injection process (tunnel emission) temperature does not affect the mechanism of injection and hence the breakdown field fairly remains constant in the tunnel emission dominated

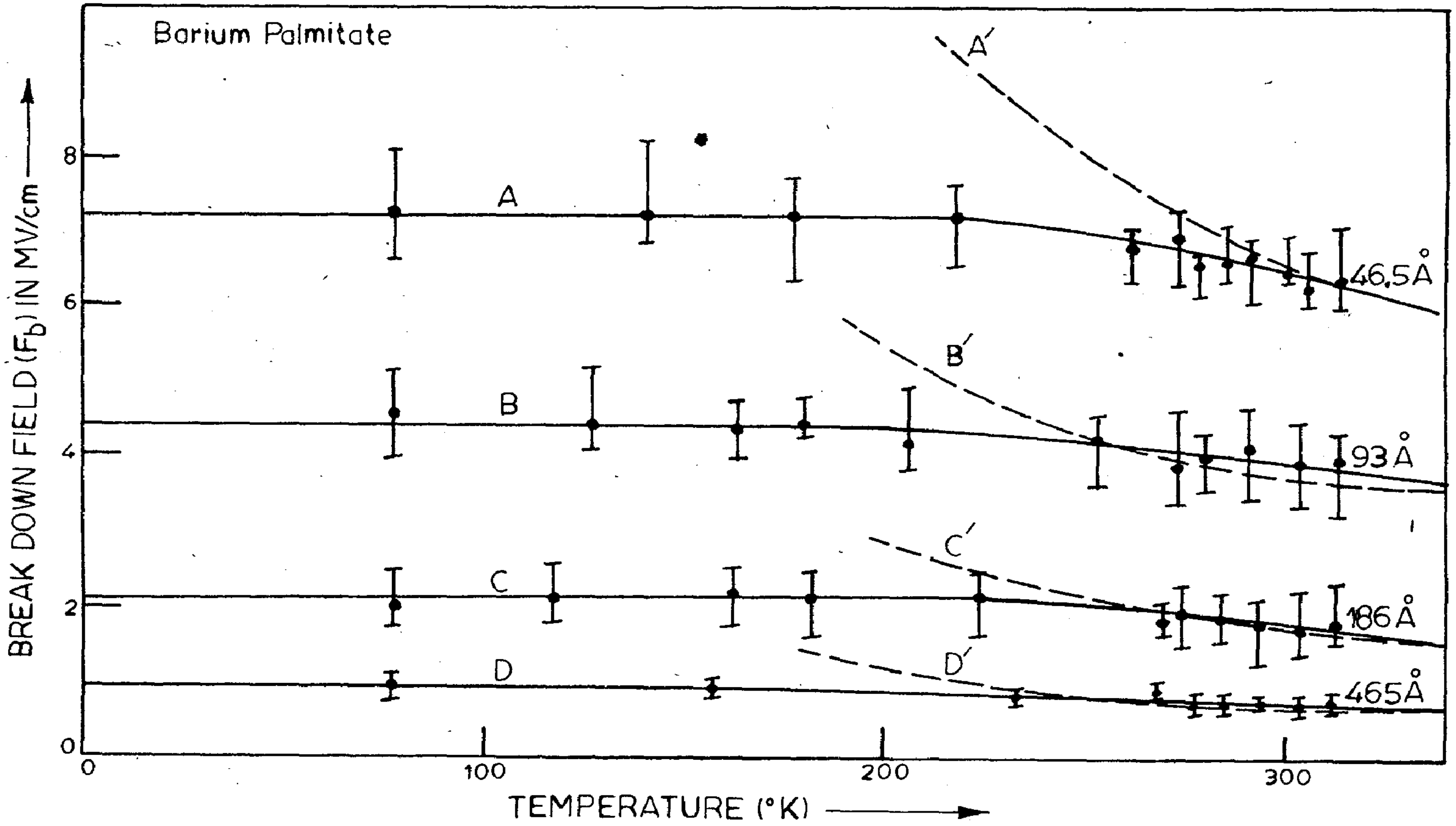


FIG.16.D.C.Breakdown field as a function of temperature.

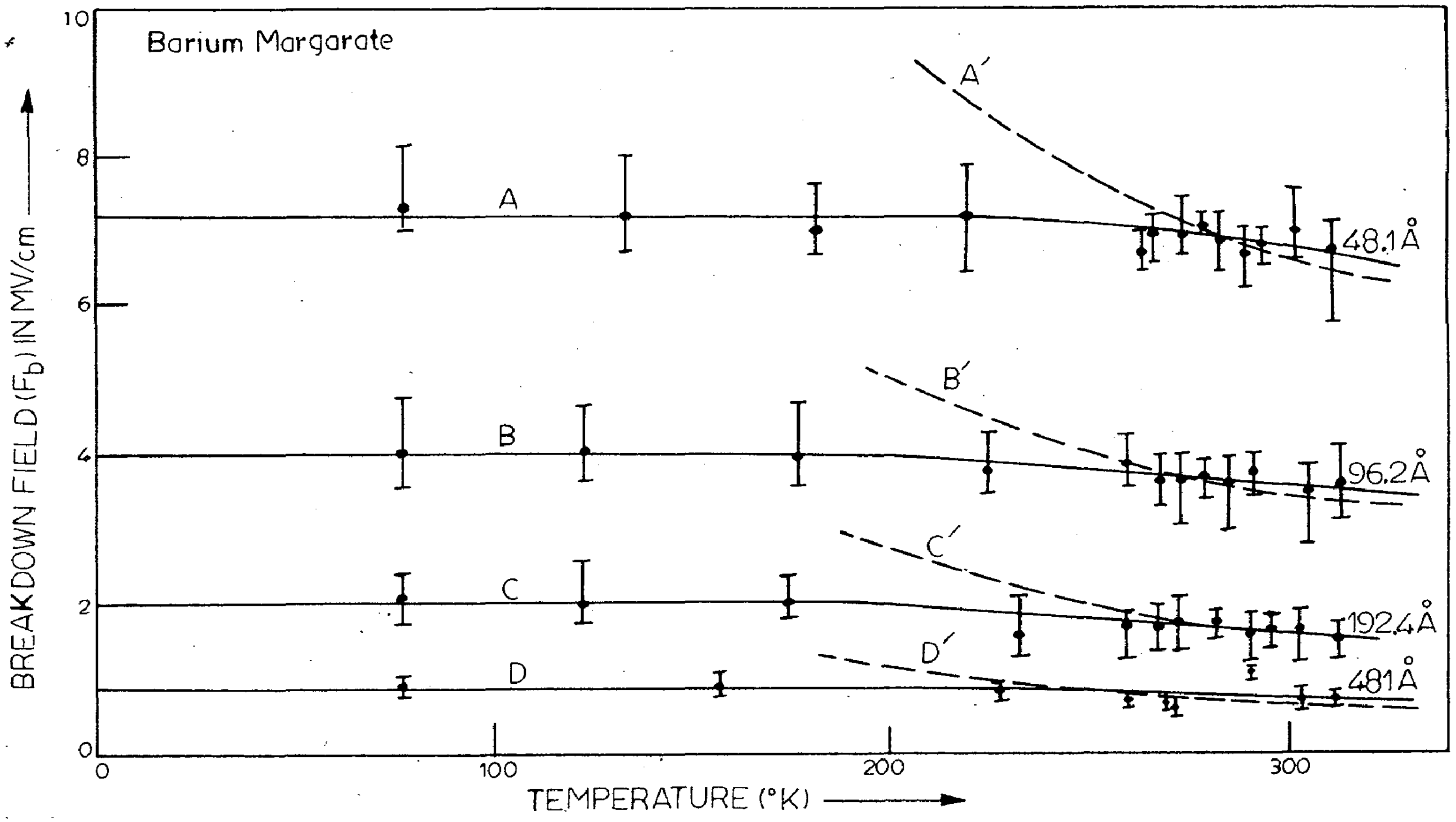


FIG.17- D.C.Breakdown field as a function of temperature.

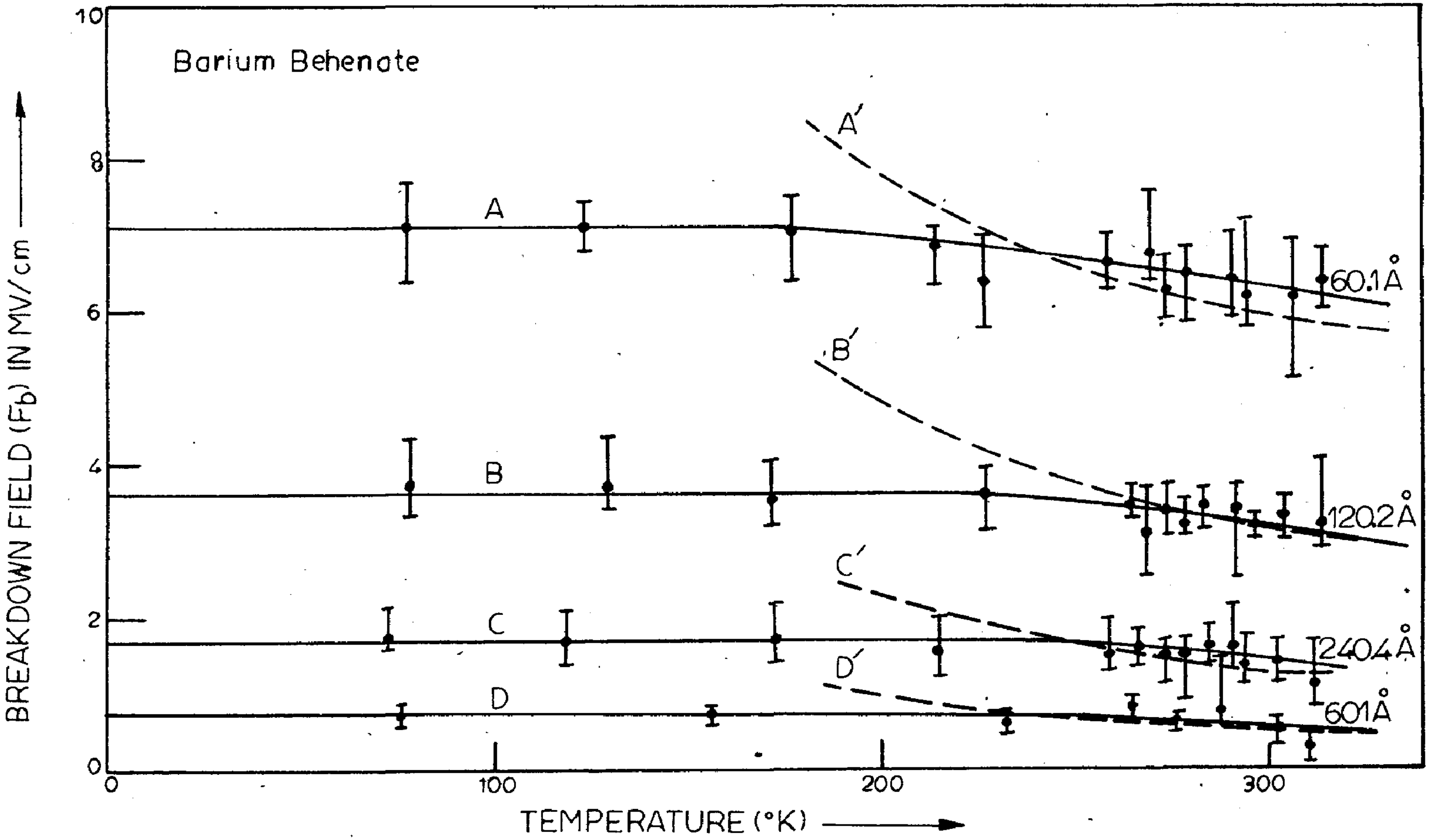


FIG.19_ D.C.Breakdown field as a function of temperature.

temperature range. The values of the monolayer thicknesses of the 'built-up' films used here have been given in Table 1. Similar curves between the 'onset' breakdown field (F_b) and the temperature have also been plotted for the 'built-up' films of barium margarate (n=17), stearate (n=18) and behenate (n=22) and the behaviour of a.c. onset breakdown field in each substance is shown in labelled figures 17,18 and 19 respectively.

As is clear from these figures, the onset breakdown field is virtually independent of temperature at lower temperatures below about 200°K. Above this temperature, the breakdown field is found to decrease with increasing temperature. The breakdown field was of the order of MV/cm as reported by Holt showing highly insulating nature of the 'built-up' molecular films. The scatter of the experimental data about the mean values of a few number of observations have been shown in all the graphs by vertical bars. To determine the scatter, a number of observations have been made at the same temperature and for the same film thickness of different samples of the same substance. The dots in the experimental plots correspond to the mean values of few observations taken under similar conditions. The variation of the 'onset' breakdown field over the entire temperature range for various film thicknesses is given in Table II.

(b) Current-Voltage Characteristics

The typical current voltage characteristics of all the four substances in the nondestructive phase have been shown in well labelled and self-explanatory figures 20 to 23. After the onset of breakdown, indicated by an abrupt rise in the current, linearly rising voltage across the film capacitor was continued till the voltage collapses and the destruction of the film commences. Before the onset of breakdown had occured, the current flowing in the circuit was very feeble. This value of current has not been recorded and the curves have been plotted starting from onset breakdown voltage. Near the destructive breakdown voltages, currents could not be recorded very properly due to the fluctuations and hence the curves are plotted only in the nondestructive phase. The V-J curves (figs. 20-23) are the representative ones and have been plotted for 4 and 20 layers of each substance with temperature as the parameter. The curves have also been drawn with a resistance in series with the film capacitor and voltage source. The point 'a' in each curve corresponds to the initial abrupt rise in the current, yielding onset of breakdown voltage. The current-density 'J'has been calculated by dividing the current(I) flowing in the circuit by the area (A) of the film capacitor. The results have been summarised in Table III.

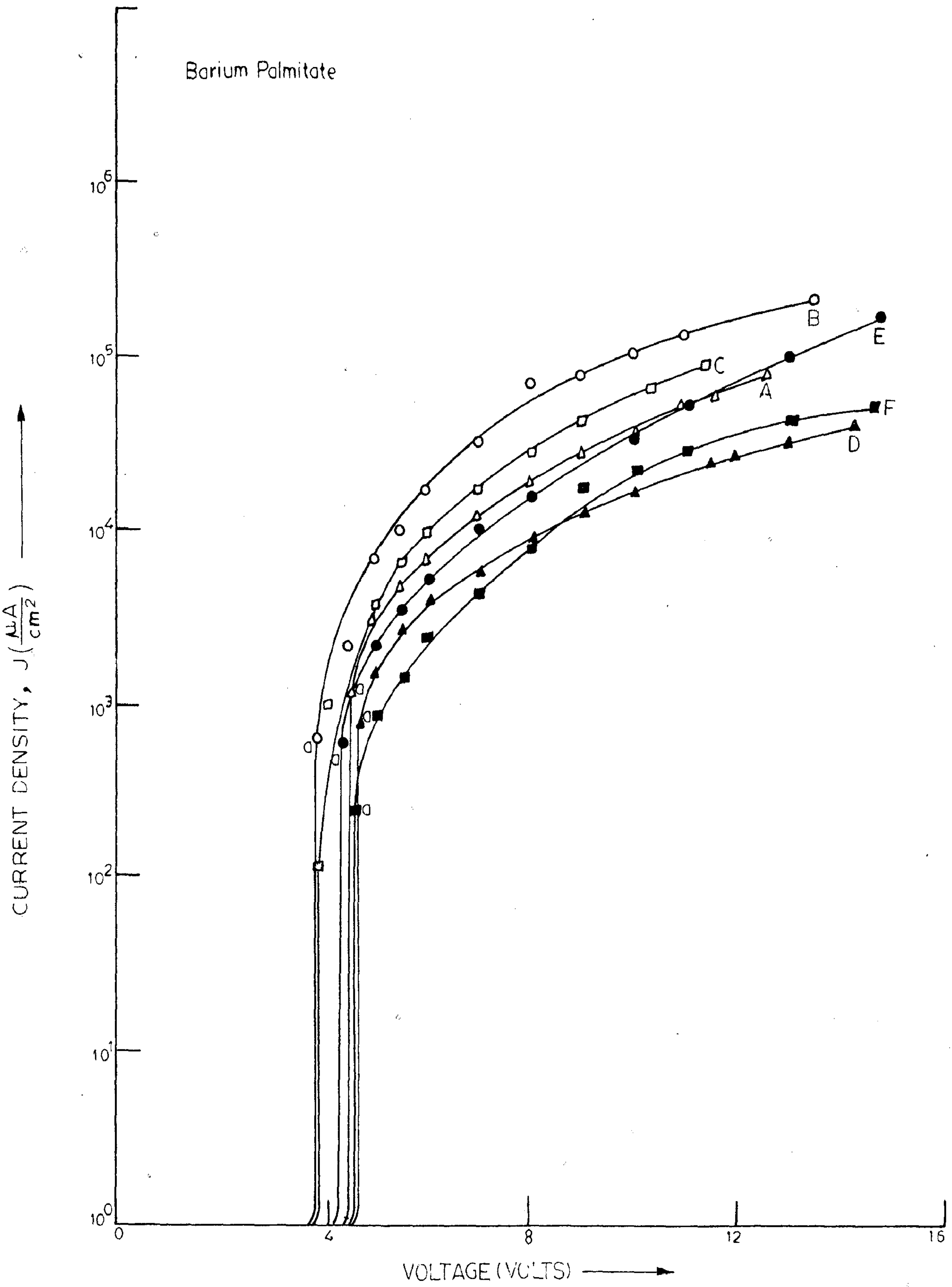


FIG.20 V-J characterstics of Barium Palmitate film.

—△— At 77°K (4 Layers)

—○— At 291°K (4 Layers)

—□— At 291°K (4 Layers)
(with a series resistor = 4.7 K)

—▲— At 77°K (20 Layers)

—●— At 291°K (20 Layers)

—■— At 291°K (20 Layers)
(with a series resistor = 4.7 K)

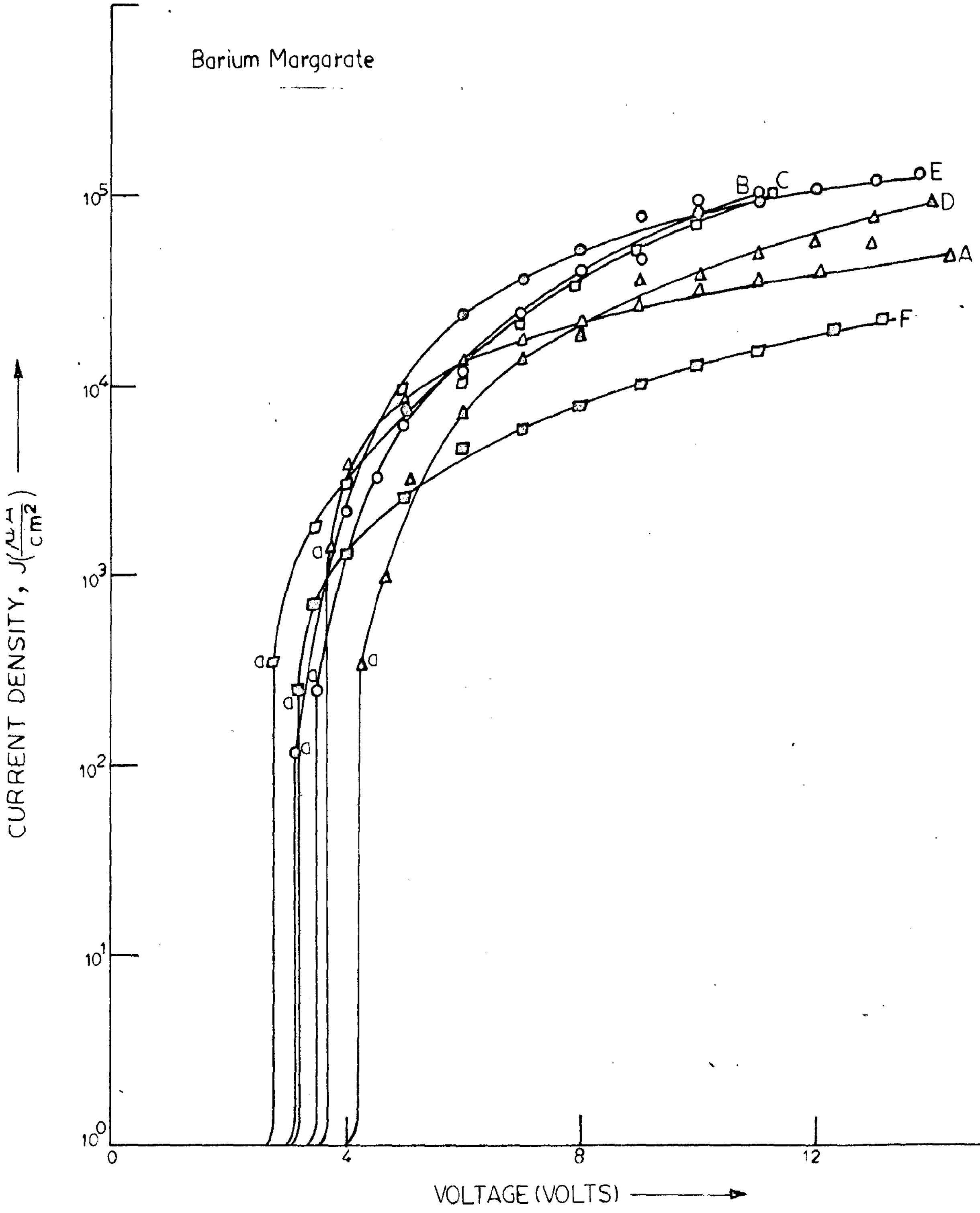


FIG.21_V-J characterstics of Barium Margarate film.

—△— At 77°K(4 Layers)

—▲— At 77°K(20 Layers)

—○— At 291°K(4 Layers)

—◎— At 291°K(20 Layers)

—□— At 291°K(4 Layers) (with a series resistor = 4.7K)

—▣— At 291°K(20 Layers) (with a series resistor = 4.7K)

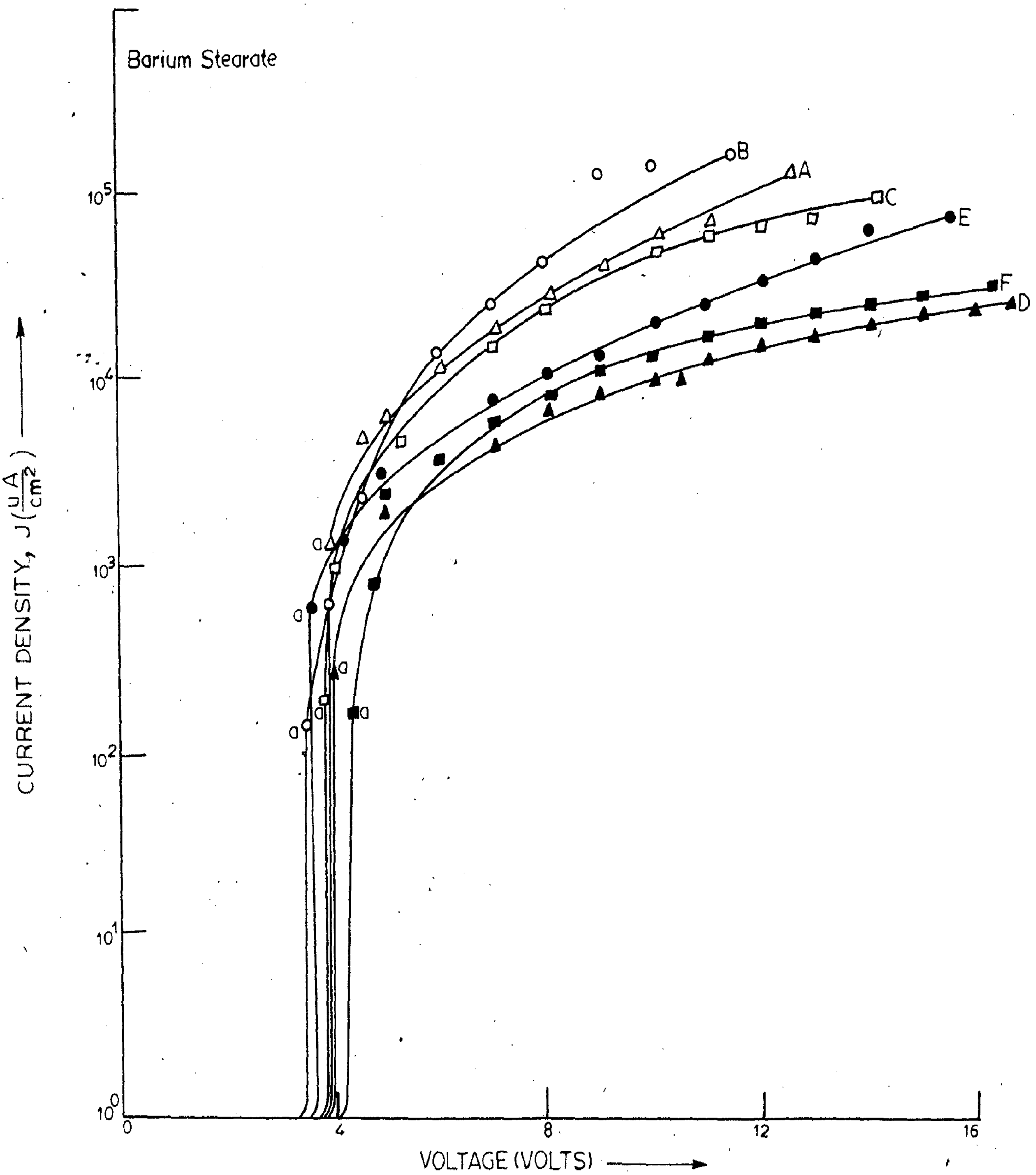


FIG.22. V-J characterstics of Barium Stearate film.

—△— At 77°K (4 Layers)
—○— At 291°K (4 Layers)
—□— At 291°K (4 Layers) (with series resistor = 4.7 K)
—▲— At 77°K (20 Layers)
—●— At 291°K (20 Layers)
—■— At 291°K (20 Layers) (with series resistor = 4.7 K)

(c) Destructive Breakdown Field

Measurements of the temperature dependence of the d.c. destructive breakdown voltage (V_{db}) have been carried out for all the four types of 'built-up' Langmuir films in the range from liquid nitrogen temperatures upto the room temperature. At this voltage, a large area of the capacitor gets destroyed. Figures 24, 25, 26 and 27 give the best fit curves of the destructive breakdown field as a function of temperature for different thicknesses of the films of barium palmitate, margarate, stearate and behenate respectively. Here, also the dots correspond to the mean values of few observations taken at the same temperature with the films of same thickness possessing almost same capacitor area and deposited under similar conditions. The relationship between dots and bars is the same as stated for the case of 'onset' breakdown. The results have also been given in Table IV.

(d) Optical Microscopic Examination of Destructive Breakdown

An optical microscopic study of the destruction of the 'built-up' film system under high electrical stresses has been made on a large number of capacitors by keeping them under a suitable microscope with a camera attachment. It was observed that the destruction of the film readily commences after the threshold voltage (V_{db}) and no destruction is seen for voltages lesser than V_{db}. A number of

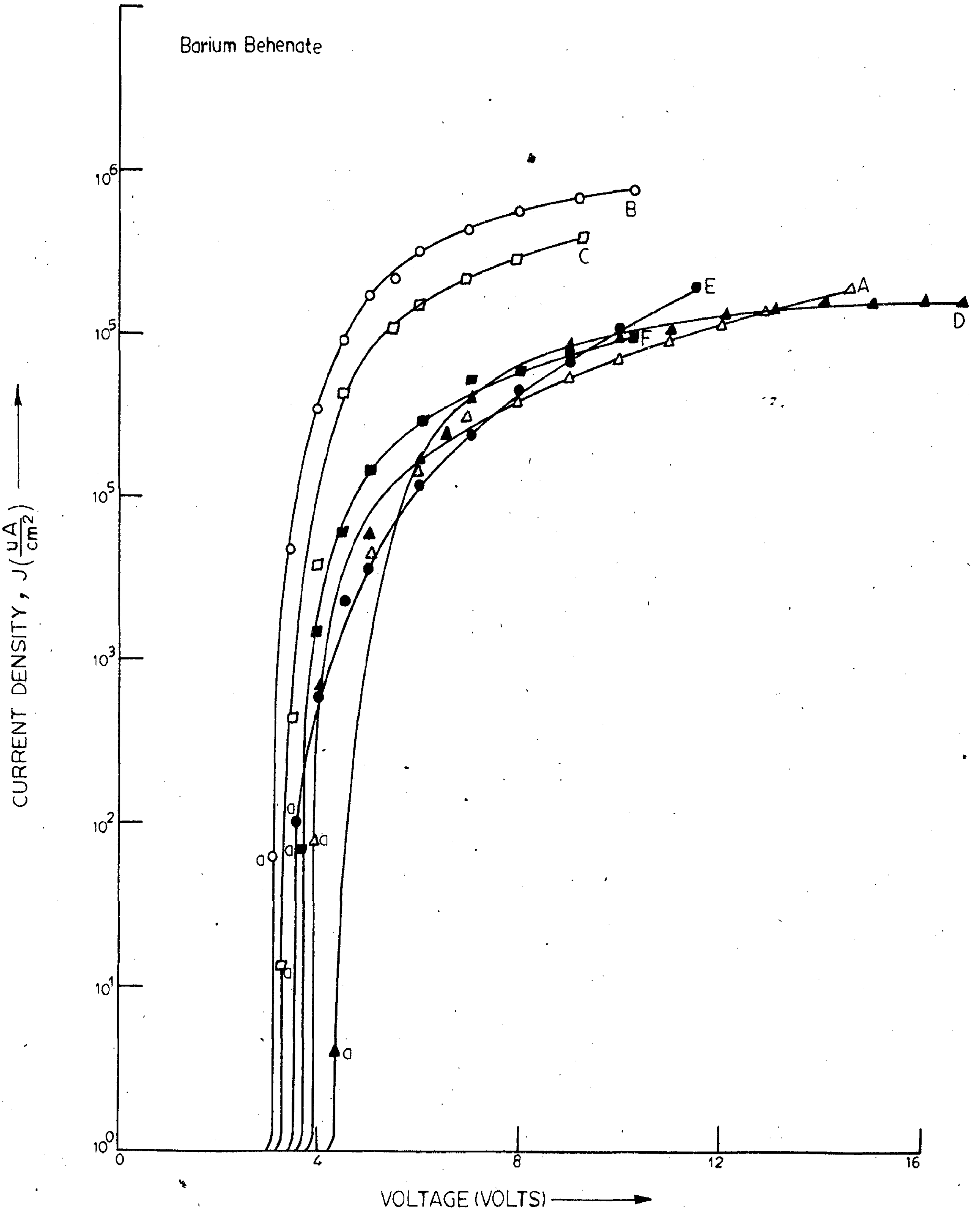


FIG.23 V-J characterstics of Barium Behenate film .

—△— At 77°K (4 Layers)

—▲— At 77°K (20 Layers)

—○— At 291°K (4 Layers)

—●— At 291°K (20 Layers)

—□— At 291°K (4 Layers)
(with series resistor = 4.7 K

—■— At 291°K (20 Layers)
(with series resistor = 4.7K)

(c) Destructive Breakdown Field

Measurements of the temperature dependence of the d.c. destructive breakdown voltage (V_{db}) have been carried out for all the four types of 'built-up' Langmuir films in the range from liquid nitrogen temperatures upto the room temperature. At this voltage, a large area of the capacitor gets destroyed. Figures 24, 25, 26 and 27 give the best fit curves of the destructive breakdown field as a function of temperature for different thicknesses of the films of barium palmitate, margarate, stearate and behenate respectively. Here, also the dots correspond to the mean values of few observations taken at the same temperature with the films of same thickness possessing almost same capacitor area and deposited under similar conditions. The relationship between dots and bars is the same as stated for the case of 'onset' breakdown. The results have also been given in Table IV.

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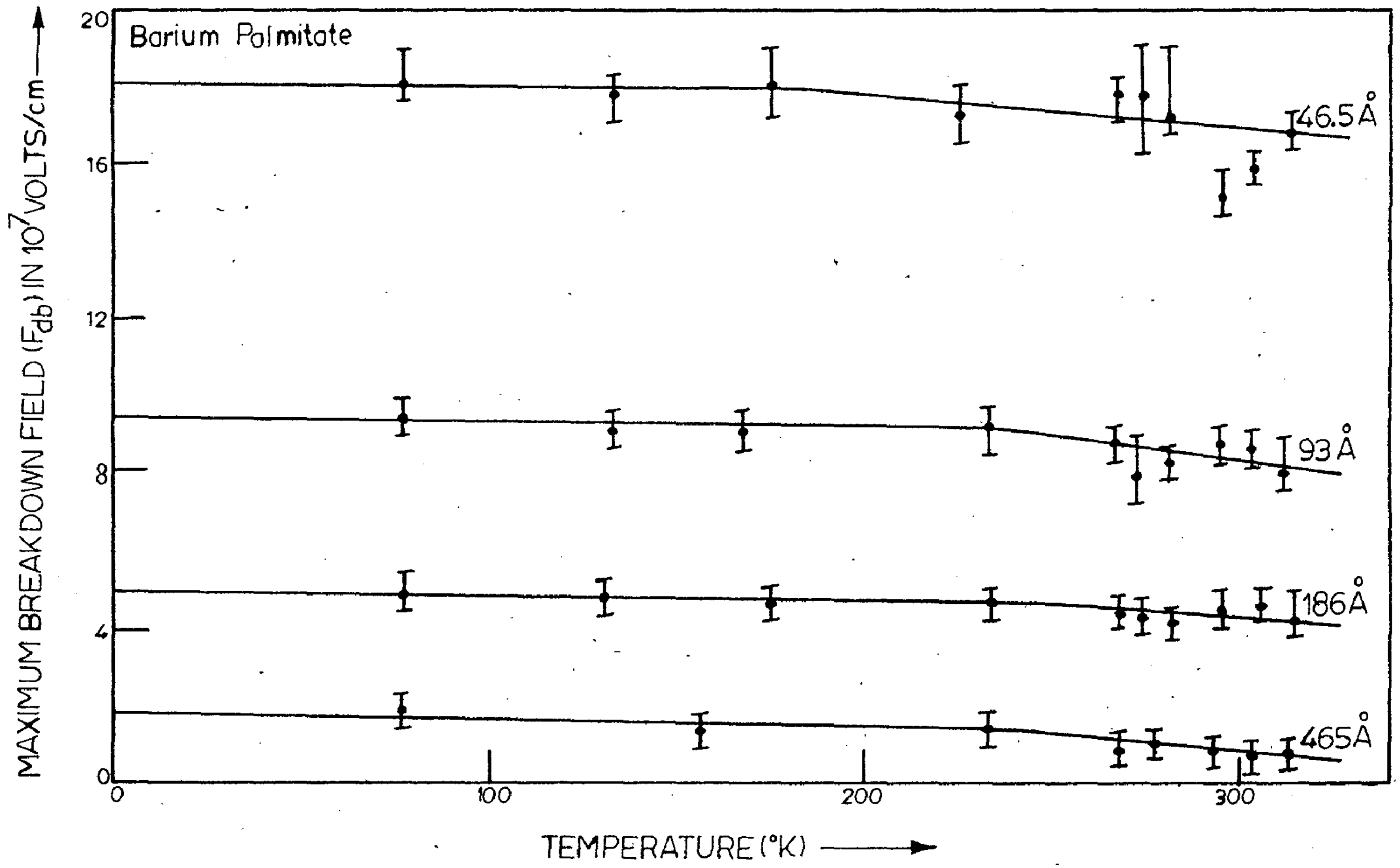


FIG.24. Destructive Breakdown field as a function of temperature.

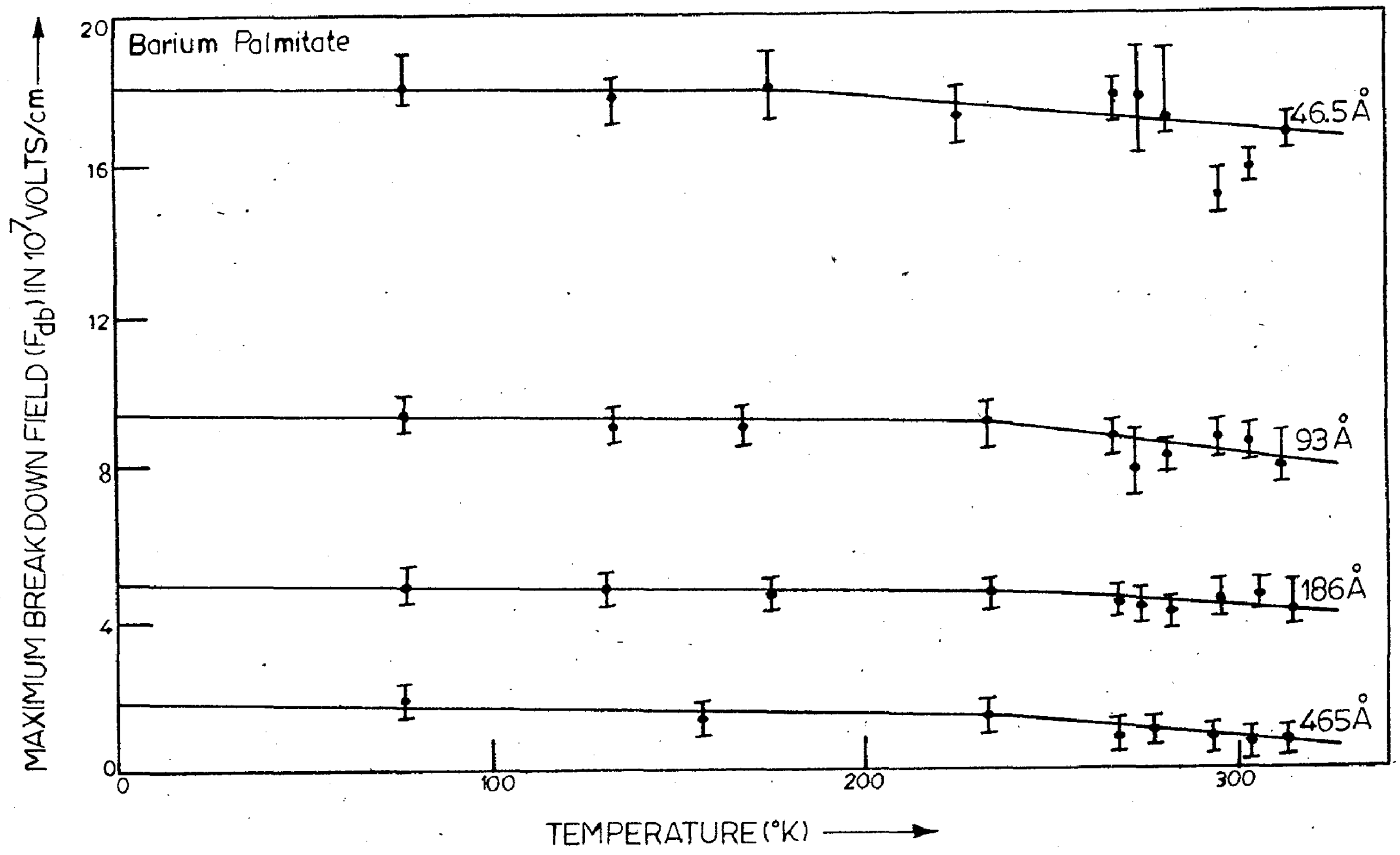


FIG.24. Destructive Breakdown field as a function of temperature.

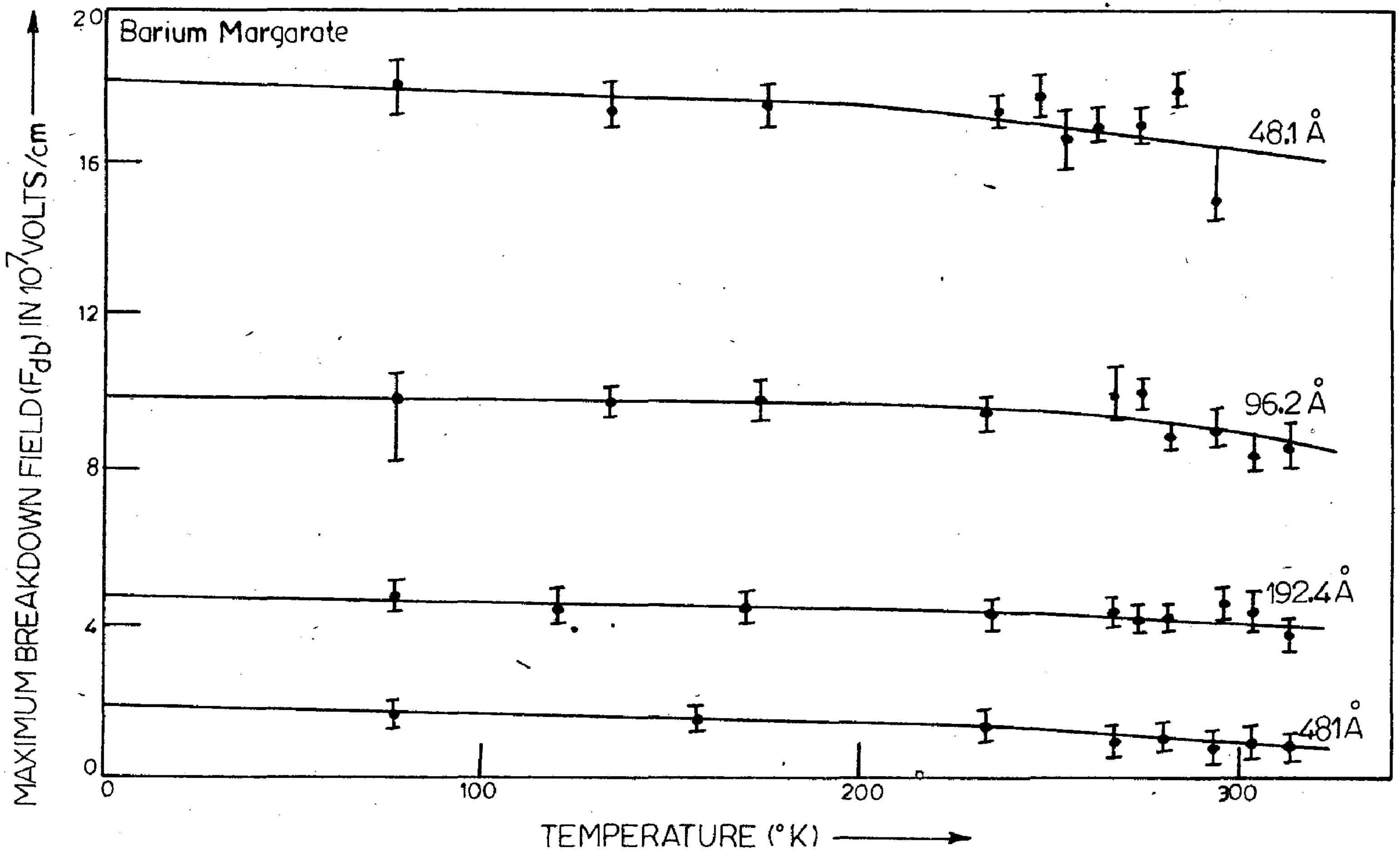


FIG.25_ Destructive Breakdown field as a function of temperature.

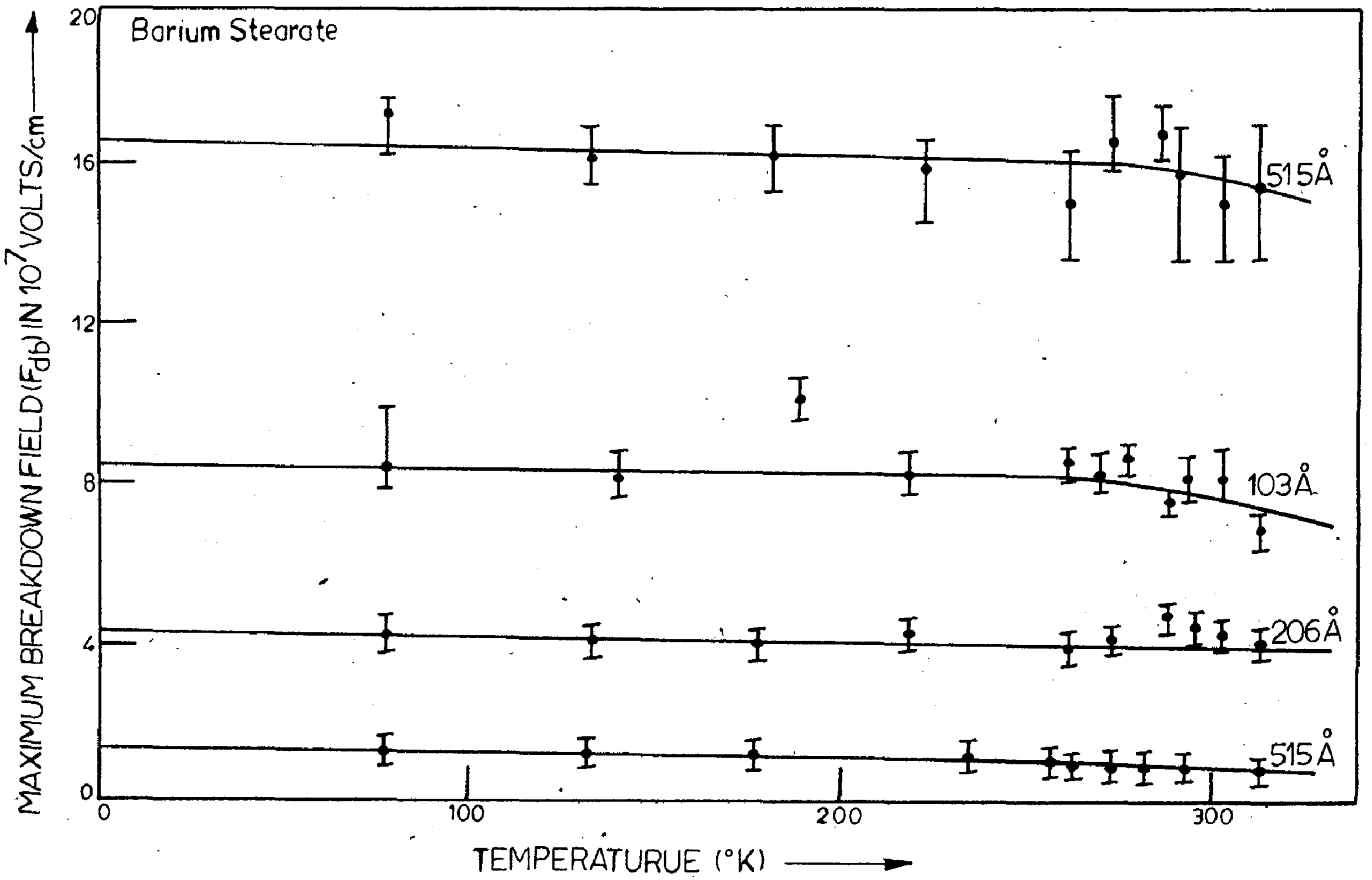


FIG.26 Destructive Breakdown field as a function of temperature.

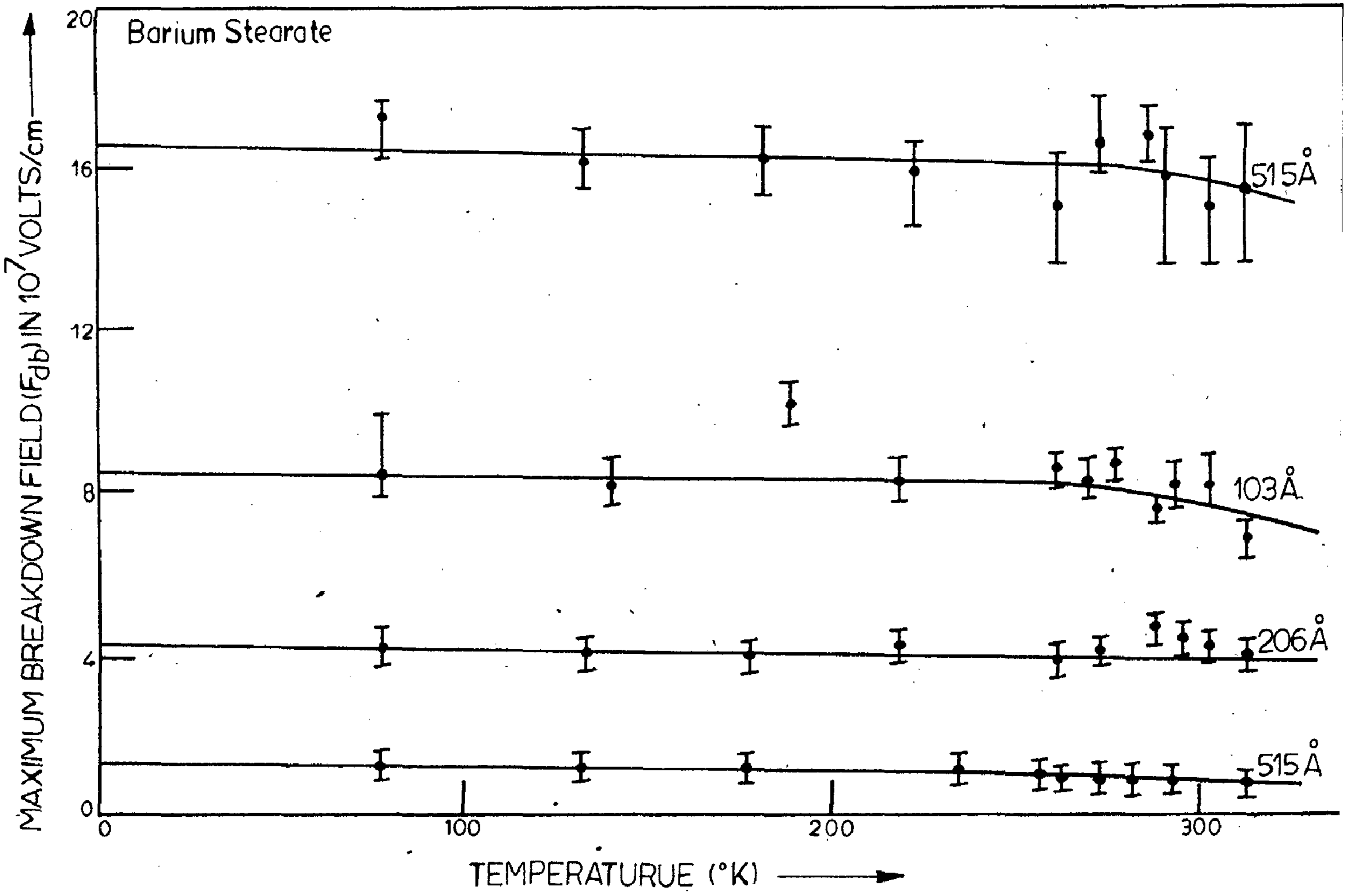


FIG.26_ Destructive Breakdown field as a function of temperature.

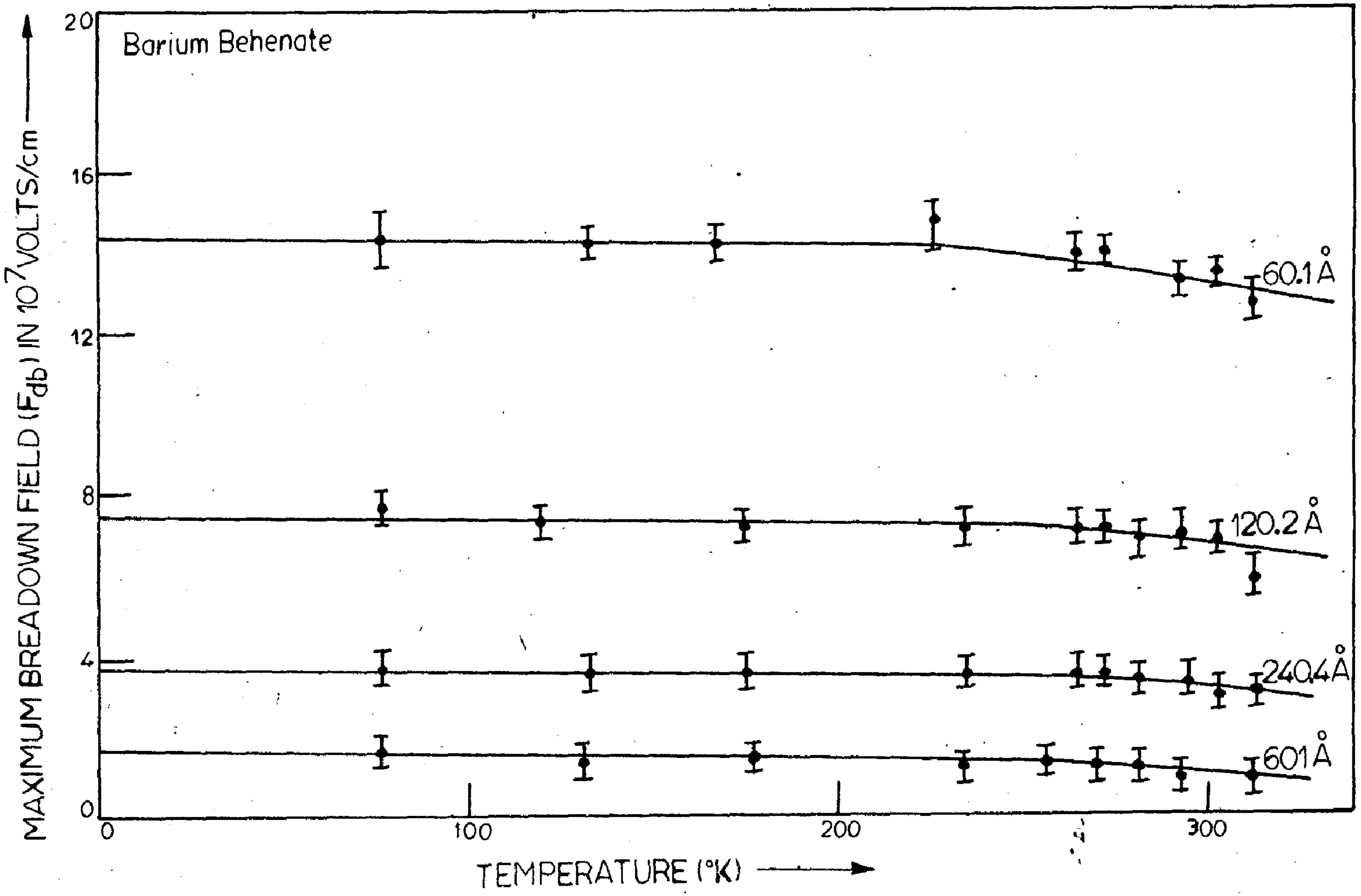
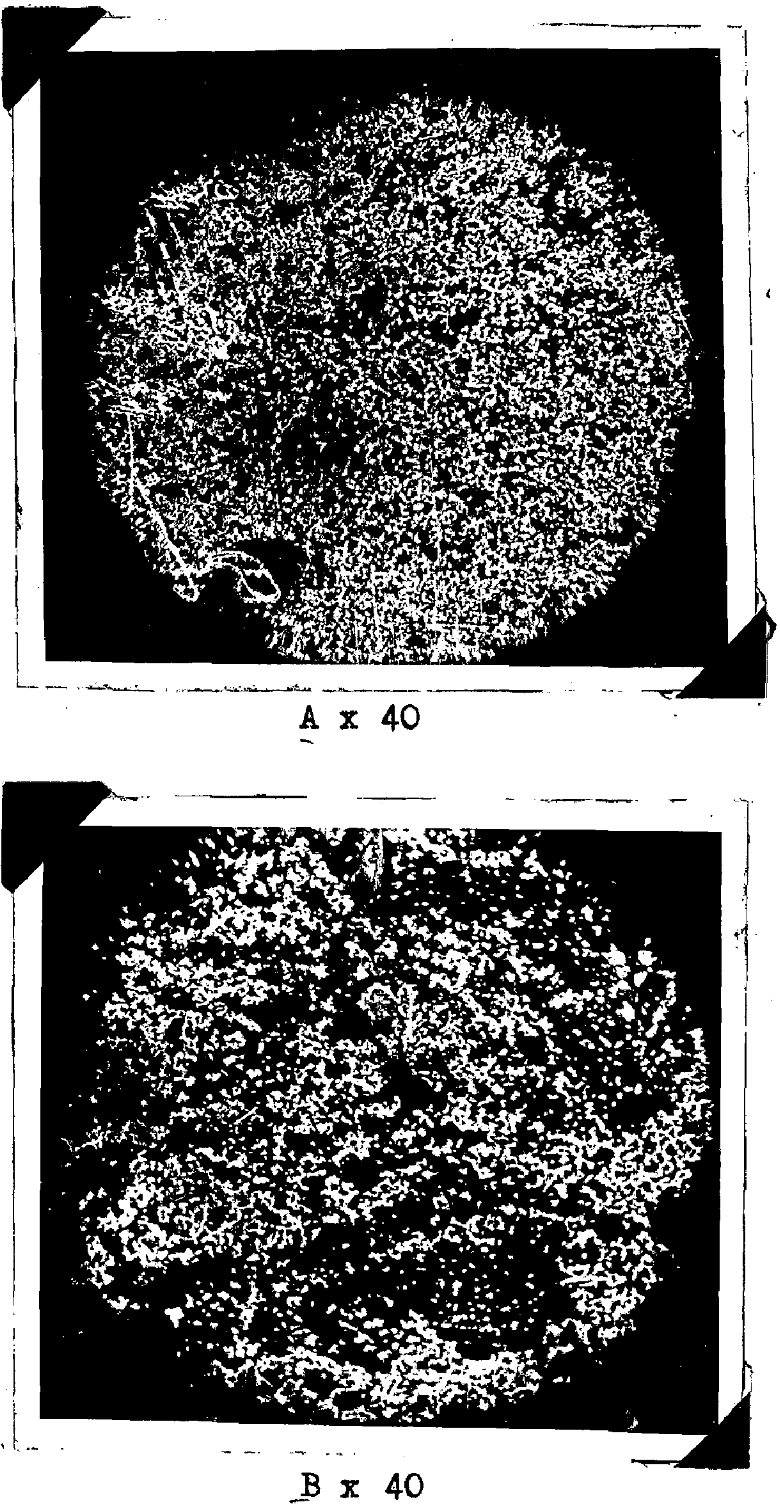


FIG.27_ Destructive Breakdown field as a function of temperature.

photographs are included to illustrate the nature of the breakdown patterns. Both transmitted and reflected light were used to capture a maximum amount of detail. Some representative transmission and reflection photomicrographs showing destruction of the film capacitors of barium palmitate, margarate, stearate and behenate, over large areas, have been shown in figures 28 to 43. The photomicrographs did not show the occurrence of 'single holes' and 'propagating breakdowns' as observed by Klein and his coworkers in his studies on evaporated film systems. The destruction of the film was accompanied by emission of light through sparks. The details of each photomicrograph is summarised in Table V.

6.2 DISCUSSION:COMPARISON WITH THEORY AND INTERPRETATION OF RESULTS

The phenomena of dielectric breakdown in **thin** films is though interesting but not yet fully understood and the mechanism of electrical breakdown in the dielectric films still seems to be an argument of debate for the investigators of this field. The theories of dielectric breakdown primarily distinguish three aspects:Intrinsic breakdown,thermal breakdown and Forlani's avalanche breakdown (Chapter I). First,the intrinsic breakdown is a property of an infinite dielectric immersed in a uniform electric field and the magnitude of this electric field is a function of temperature. Once the critical field is

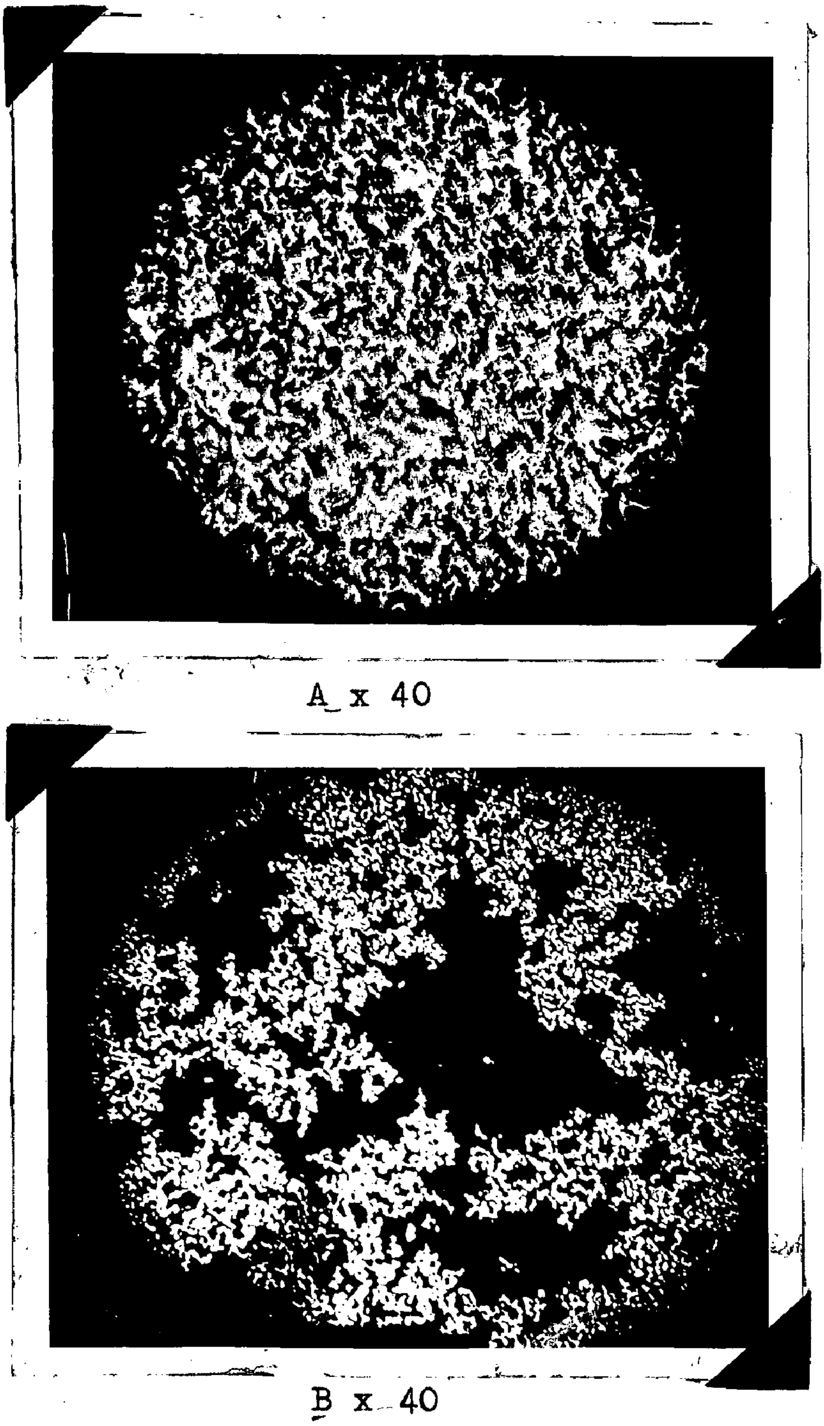


A x 40

B x 40

FIG.28- TRANSMISSION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 93 Å THICK BARIUM PALMITATE FILM TAKEN AT

(A) 77°K and (B) 291°K

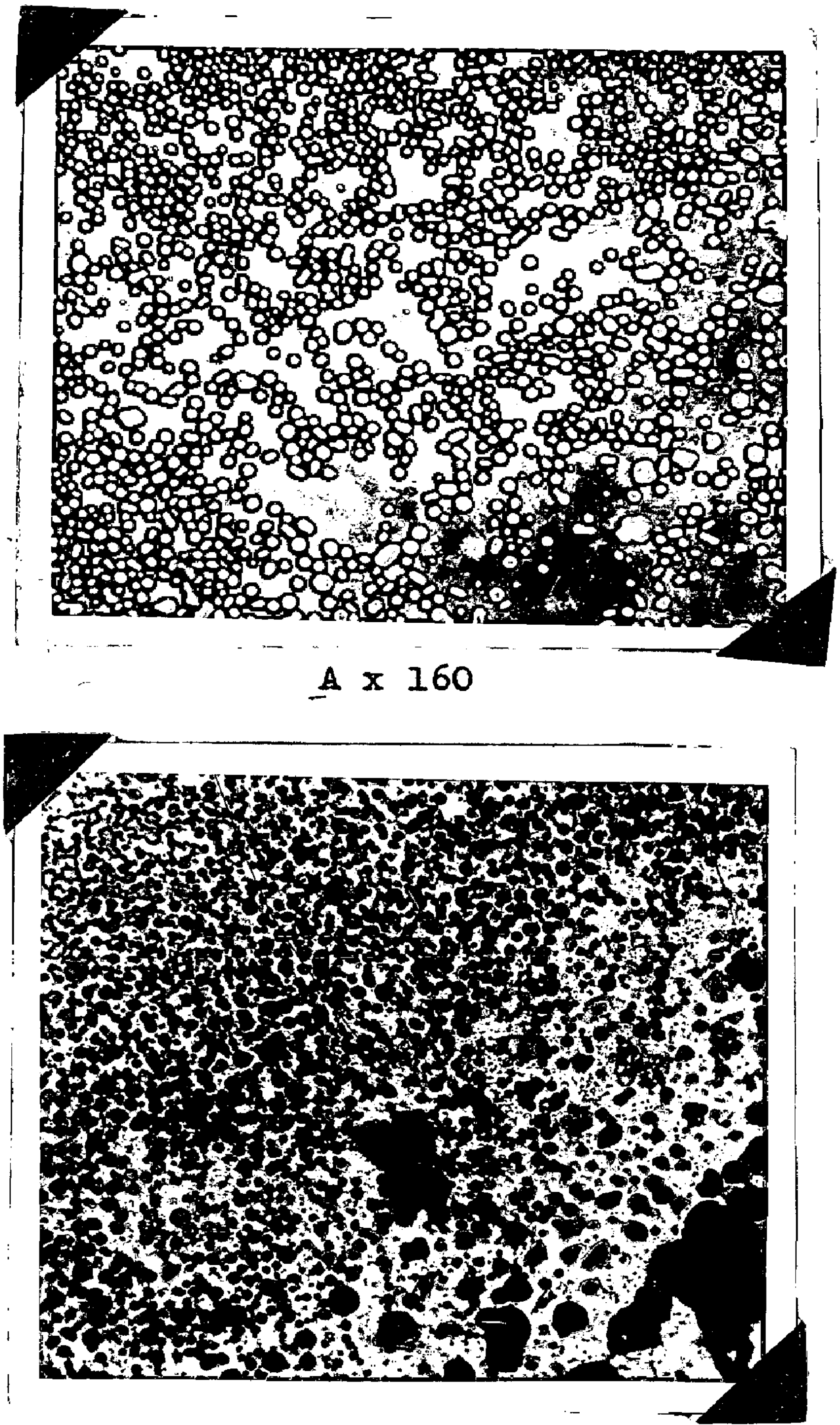


A x 40

B x 40

FIG.29- TRANSMISSION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 465 Å THICK BARIUM PALMITATE FILM TAKEN AT

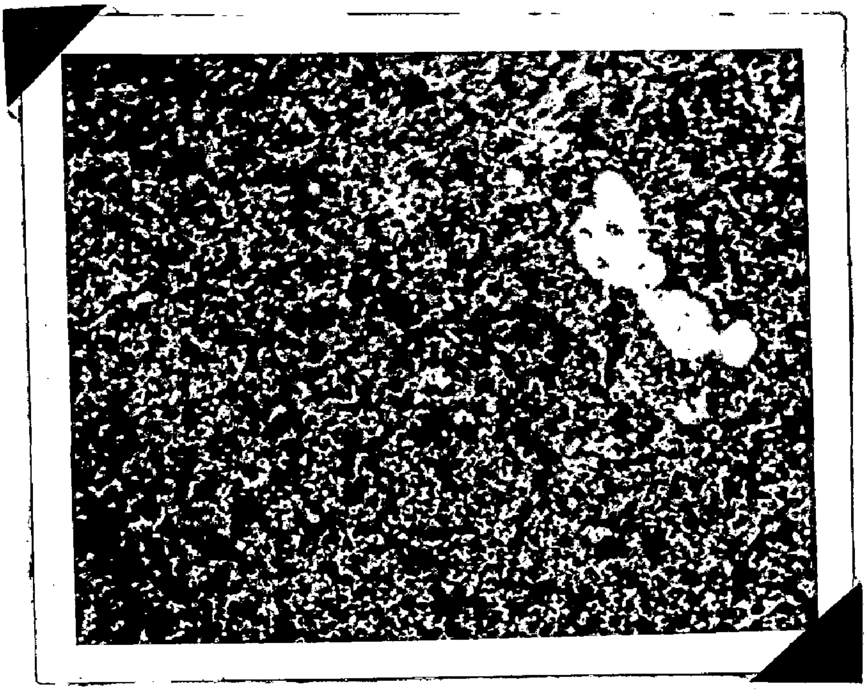
(A) 77°K and (B) 291°K



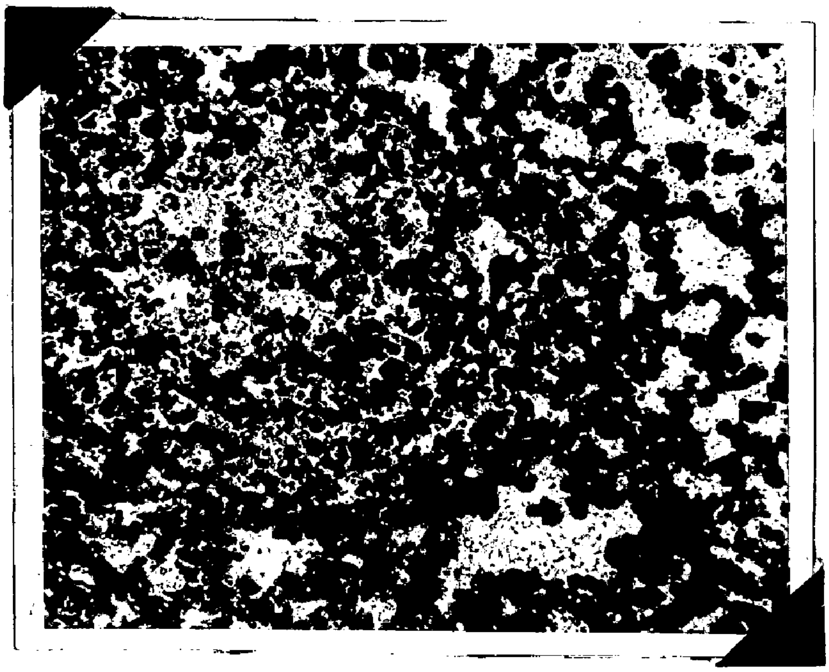
A x 160

B x 160

G.30- REFLECTION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 93 Å THICK BARIUM PALMITATE FILM TAKEN AT (A) 77°K and (B) 291°K



A x 160



B x 160

FIG.31- REFLECTION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 465 Å THICK BARIUM PALMITATE FILM TAKEN AT (A) 77°K and (B) 291°K

reached, breakdown is virtually instantaneous. In thermal breakdown processes, a gradual heating of the dielectric due to the field produced currents is obtained. At the critical field electrical energy is converted to thermal energy fast enough to cause a continuing temperature rise and eventual destruction. The last said mechanism of breakdown has been described to be due to the formation of an electron avalanche wherein carriers absorb from the electric field sufficient energy to generate other carriers which in turn generate others. This mechanism of breakdown has generally accepted to be the prime agent of electrical breakdown while the other two refer to macroscopic manifestations. The thickness dependent studies of dielectric breakdown in the present film systems as has already been reported by Agarwal and Srivastava(51,52) and the temperature dependent studies as presented here also permitted to choose the avalanche mechanism as the predominant one.

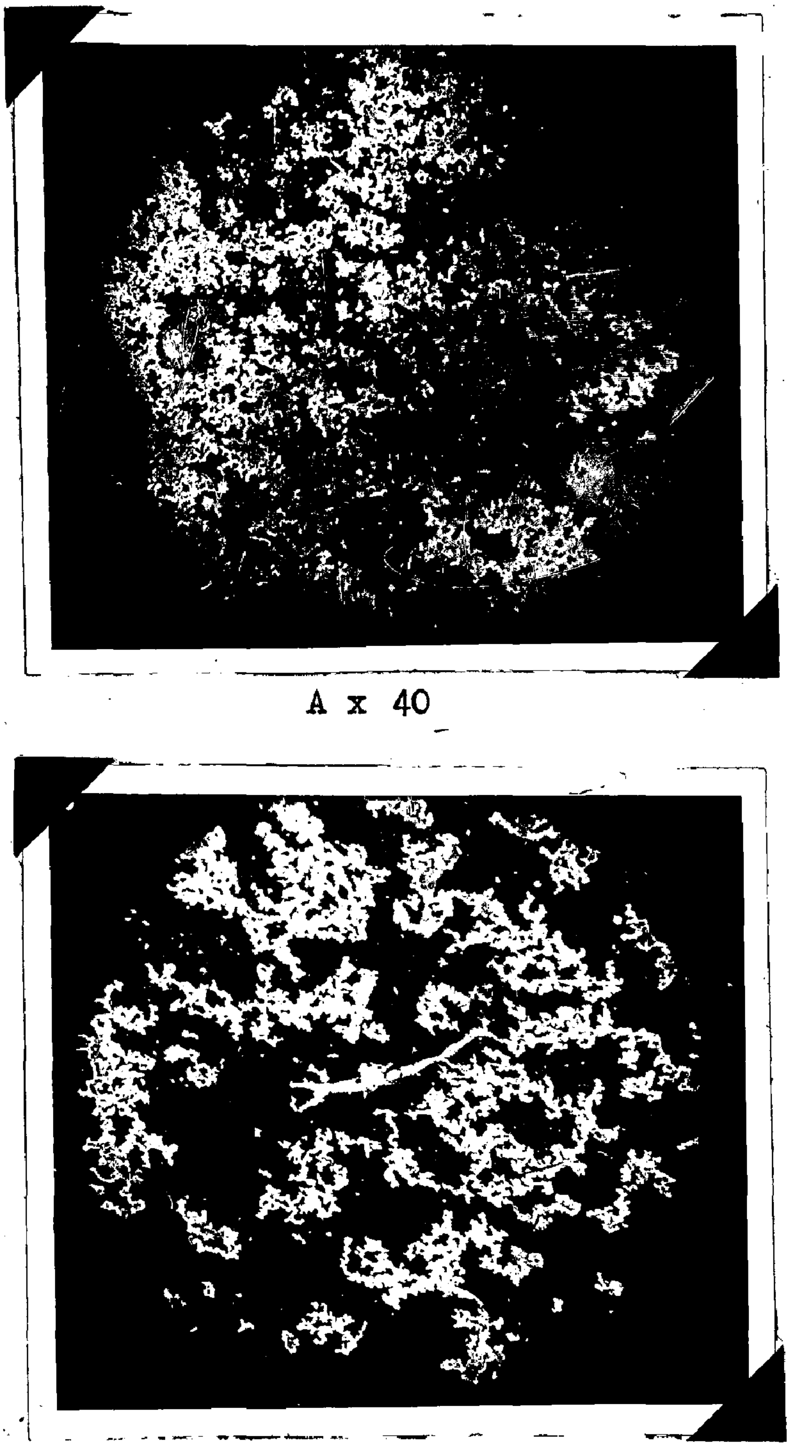
The data on temperature dependence of the breakdown field, presented in Sec.6.1 and the earlier thickness dependent studies (51,52) in 'built-up' molecular films are suitable for comparison with the various breakdown theories.The validity of the above referred types of breakdown with reference to the present film system is critically examined here.

The original theories of **von** Hippel(24) and

Frohlich(25) which were later reviewed by Franz(26,227), Stratton(20) and O'Dwyer(21,27,28), ascribe breakdown in insulators to electron avalanches produced by impact ionization. These older theories established the concept of the intrinsic breakdown field which is independent of dielectric thickness, in disagreement with the present film system studied(51,52). Here, breakdown occurs at that field at which the energy gain of the conduction electrons from the field can not be balanced by phonon collisions. The breakdown field is found to depend strongly upon temperature and an increase is seen in the breakdown field with decreasing temperatures in accordance with the term $[1+2/(e^{A/T}-1)]^{-1/2}$, where A is a constant peculiar to the dielectric used(228).

A comparison of the curves (between F and T) plotted using the above relation derived from the concepts of intrinsic breakdown theories was made with those plotted using our experimental data on the 'built-up' Langmuir film system and it is seen that the theoretical curves always have a positive slope whereas the slope of the experimental curves is negative. Thus it is concluded that this intrinsic breakdown theory can not explain the breakdown in our film system.

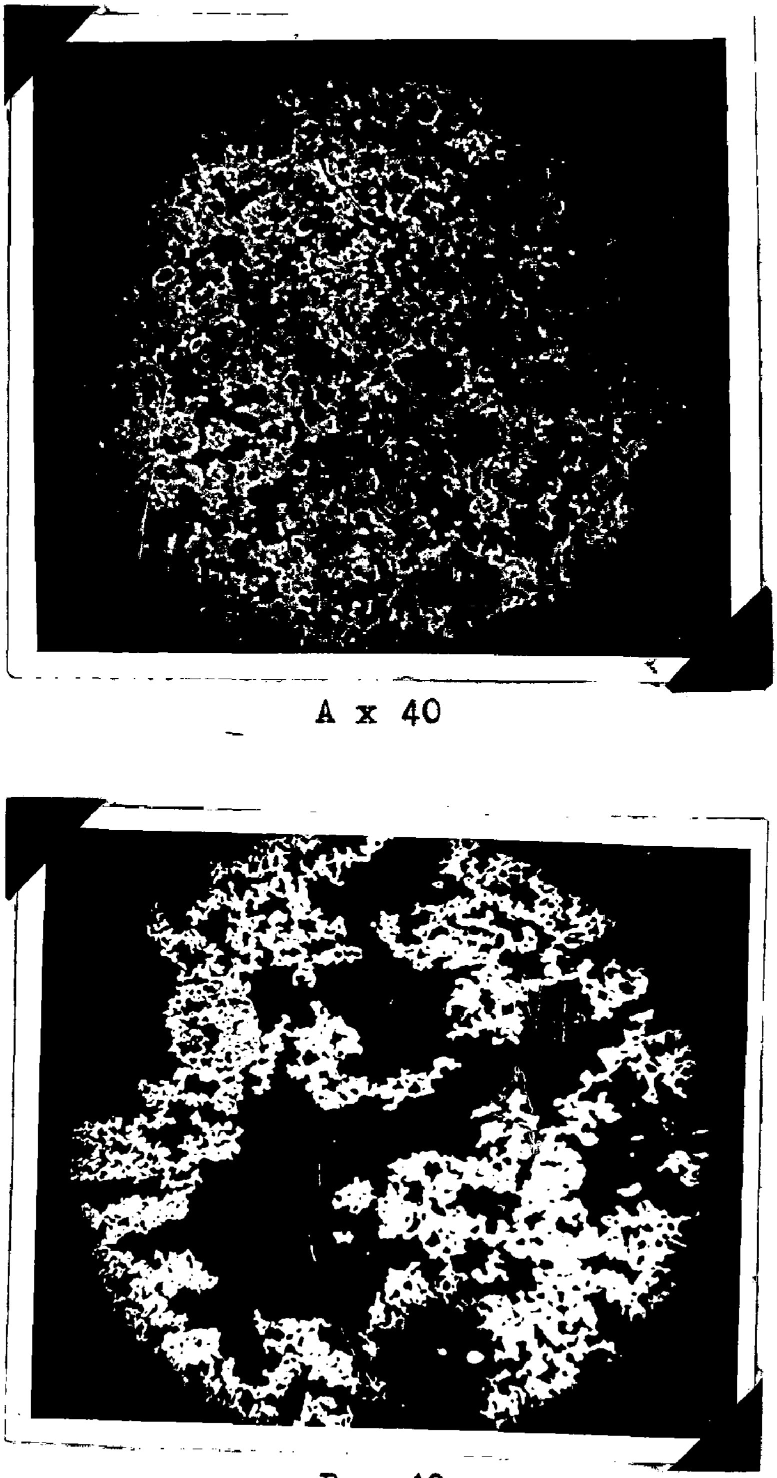
O'Dwyer(229) had also presented a theory of intrinsic breakdown in amorphous dielectrics due to Frohlich. According to this theory the electrons are assumed to be distributed over numerous energy levels in the valence-



A x 40

B x 40

FIG.32- TRANSMISSION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 96.2 Å THICK BARIUM MARGARATE FILM TAKEN AT (A) 77°K and (B) 291°K

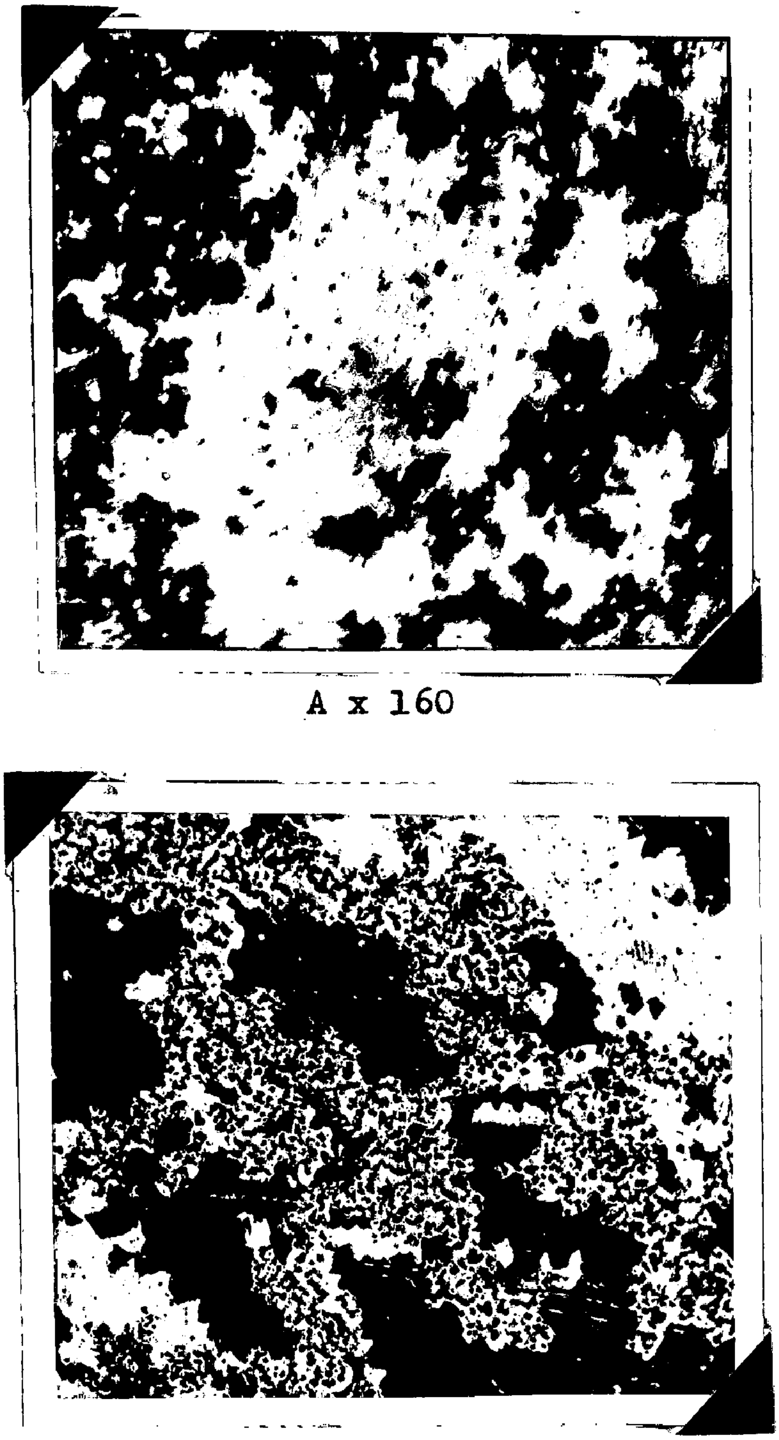


A x 40

B x 40

FIG.33- TRANSMISSION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 481 Å THICK BARIUM MARGARATE FILM TAKEN AT

(A) 77°K and (B) 291°K

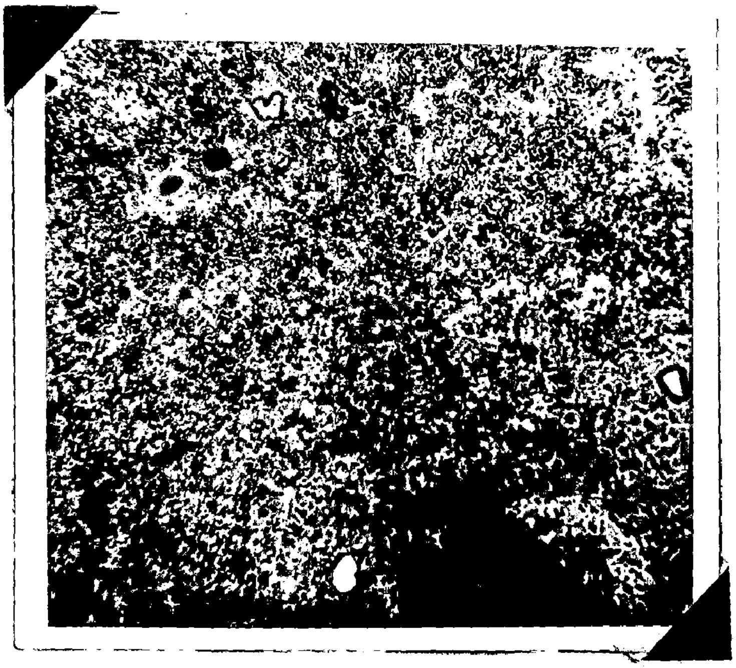


A x 160

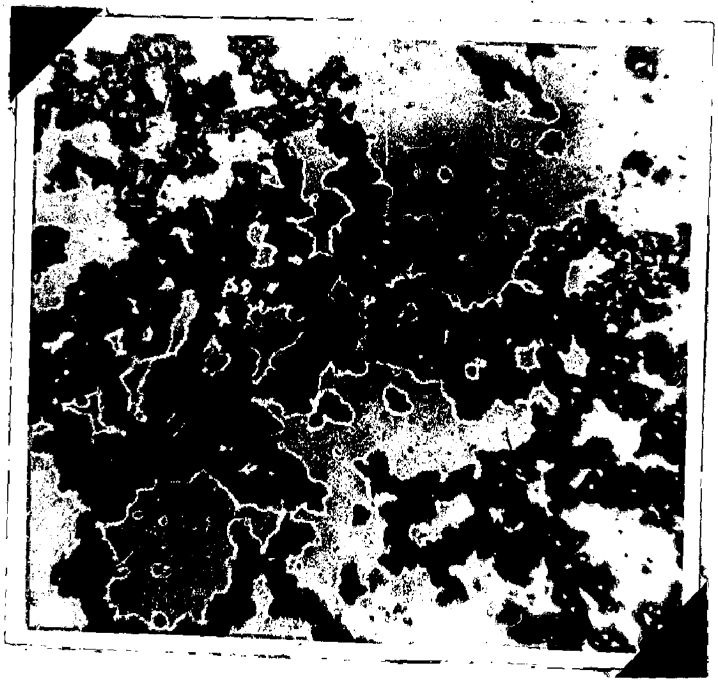
B x 160

FIG.34- REFLECTION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 96.2 Å THICK BARIUM MARGARATE FILM TAKEN AT

(A) 77°K and (B) 291°K



A x 160



B x 160

FIG.35- REFLECTION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 481 Å THICK BARIUM MARGARATE FILM TAKEN AT

(A) 77°K and (B) 291°K

conduction band gap of the dielectric.These levels are known as traps. The breakdown voltage is found to vary with temperature as $e^{\Delta V/2kT}$ where ΔV is the spread of the trap levels and k is the Boltzmann's constant.

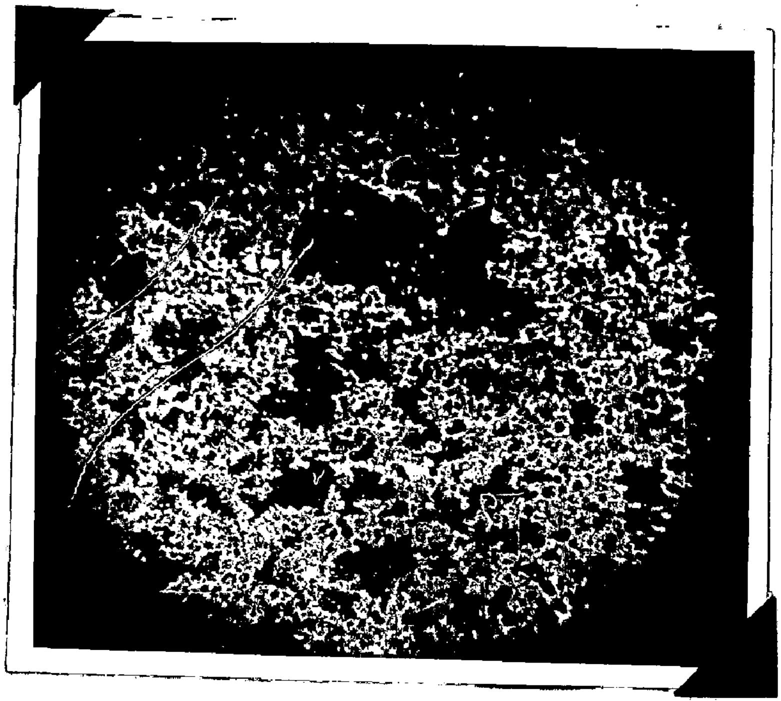
X-ray diffraction studies (203) made on the present film system shows the crystalline nature of the dielectric film. Also, Germer and Stork's(182) have shown by electron diffraction technique that the film forms uniaxial hexagonal crystals with the symmetry axis perpendicular to the plane of the film thus giving two refractive indices as observed by Blodgett and Langmuir(62). Two refractive indices of the film have also been studied by Engelson with their coworkers(230) and by Tomar and Srivastava(231). These observations show that the films studied are not amorphous and therefore the above O'Dwyer's theory is not expected to be applicable in the present case.

However, a glance at the nature of the breakdown observed seems to preclude any possibility of the breakdown occured in our film system being classified as thermal. This indication is further substantiated by the following observations.

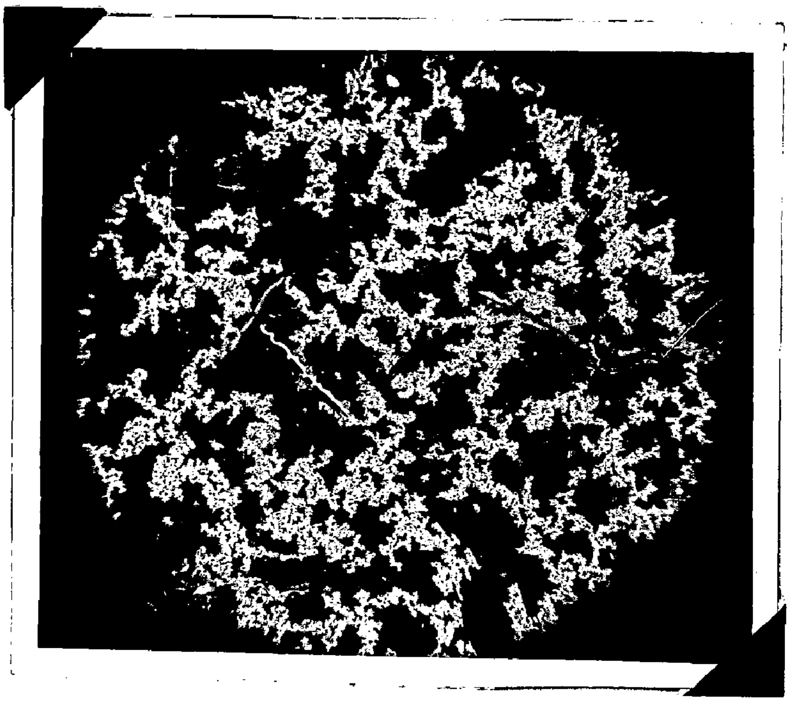
An investigation of the frequency dependence of the a.c. breakdown field has been carried out for 'built-up' film capacitors (Chapter VII). The curves (fig.48) have shown that the field increases as the frequency of the applied electrical stress is increased. Klein and

Lavenon(125) have also plotted similar curves on their specimens (SiO) fabricated on glass slides by the evaporation technique. The frequency dependence of the breakdown strength calculated on thermal breakdown theory turns out to be opposite to the one, experimentally observed here. Therefore, it is concluded that the breakdown observed here in our film system is non-thermal in nature. Agarwal and Srivastava(122) have also earlier shown the nonthermal nature of the breakdown in the present film system. Also the bendover in the current-voltage characteristics observed are found to be opposite to the one expected in the case of thermal breakdown(59). This also shows the nonthermal nature of the breakdown observed. The most successful approach seems to be that of Forlani and Minnaja(44) (Chapter I) who have recently developed a theory of breakdown in thin films. Their theory has already been supported by a number of experimental measurements taken by Budenstein et al and many other workers.

Forlani and Minnaja(40) have developed a field emission theory of dielectric breakdown assuming that the electron injected at the contacts, for sufficiently large value of the electric field, travel along the bottom of the dielectric conduction band. The main physical hypothesis of this theory is that the dielectric is an ionic crystal and the electrons are free in the conduction band of the dielectric. Particularly at low



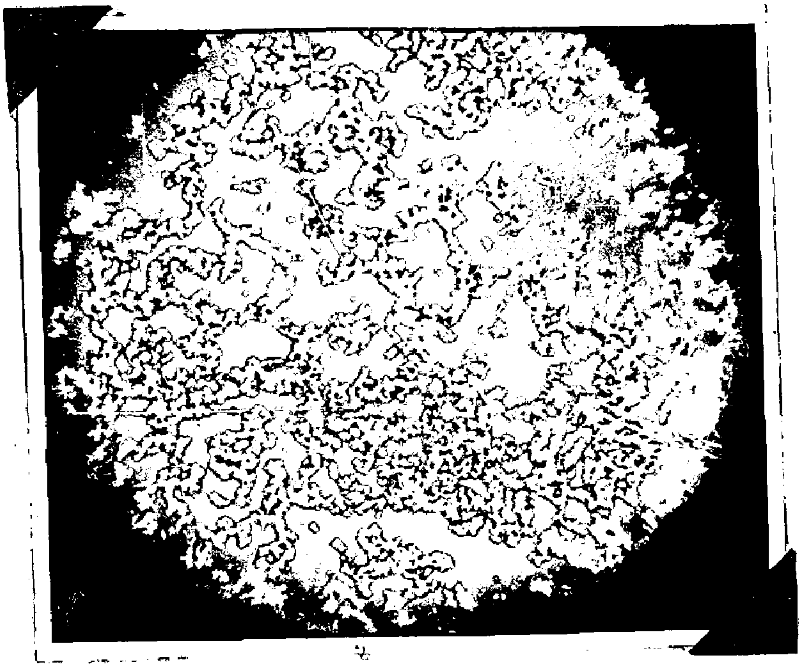
A x 40



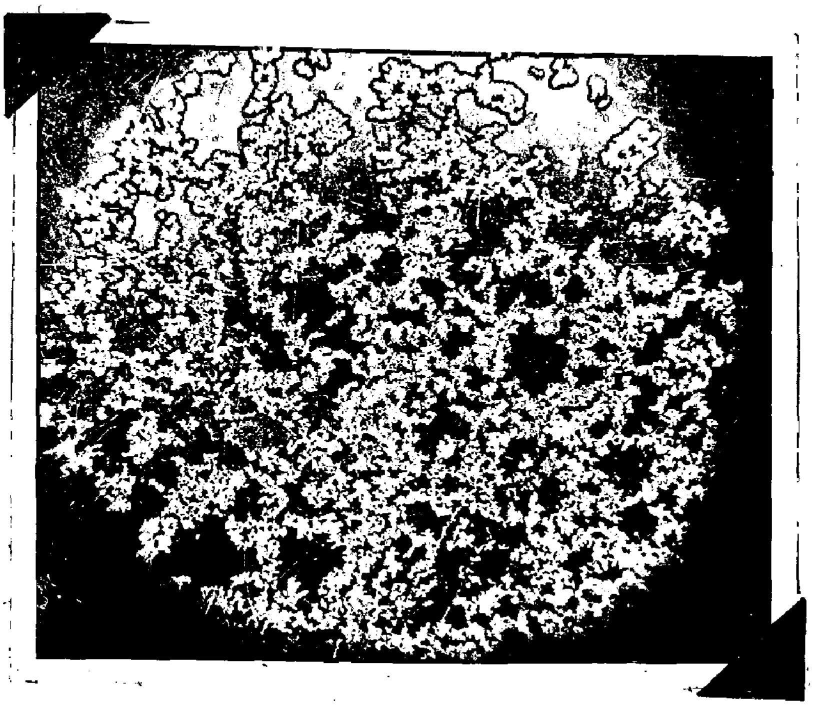
B x 40

FIG.36- TRANSMISSION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 103 Å THICK BARIUM STEARATE FILM TAKEN AT

(A) 77°K and (B) 291°K



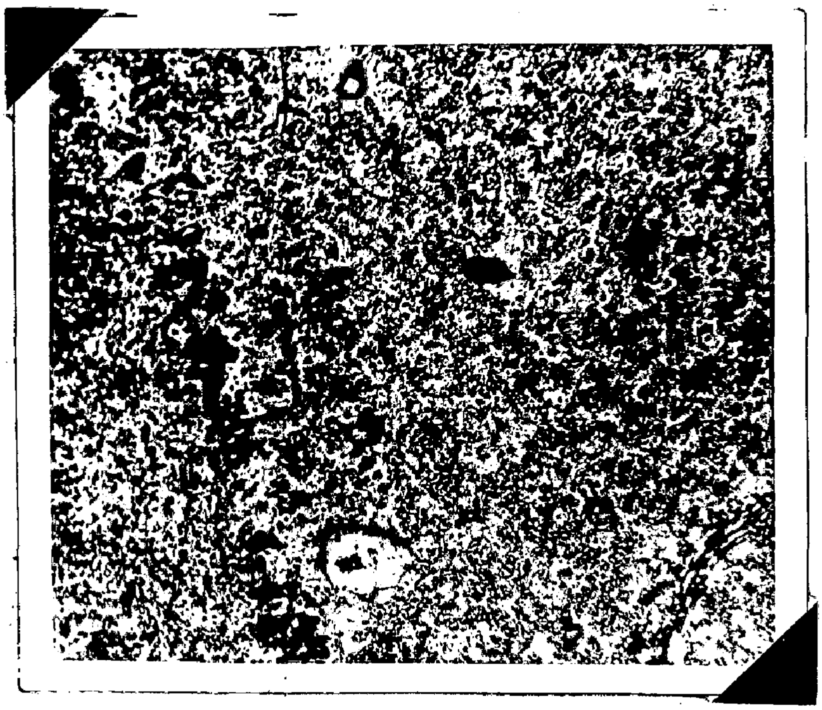
A x 40



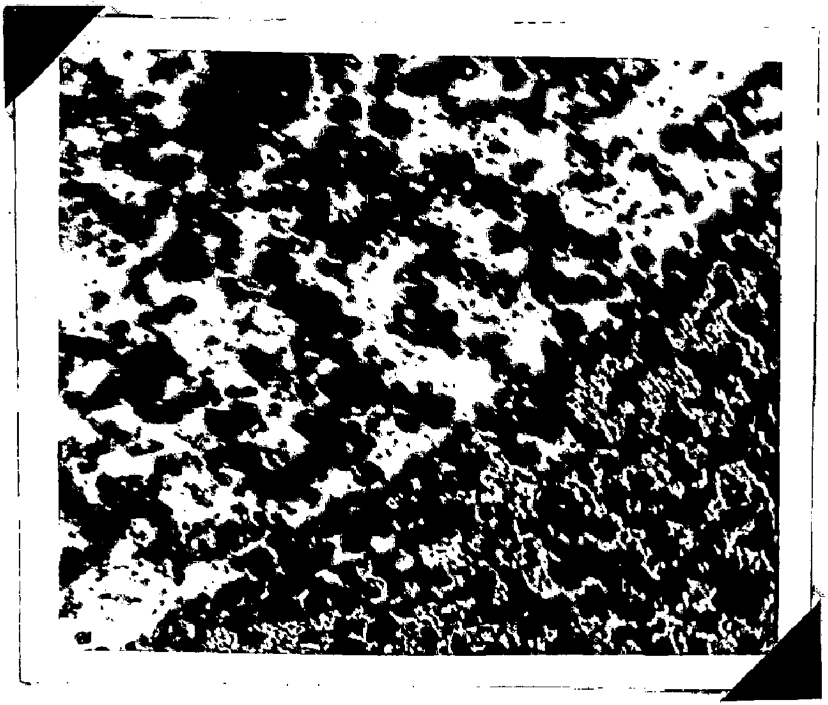
B x 40

FIG.37 - TRANSMISSION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 515Å THICK BARIUM STEARATE FILM TAKEN AT

(A) 77°K and (B) 291°K



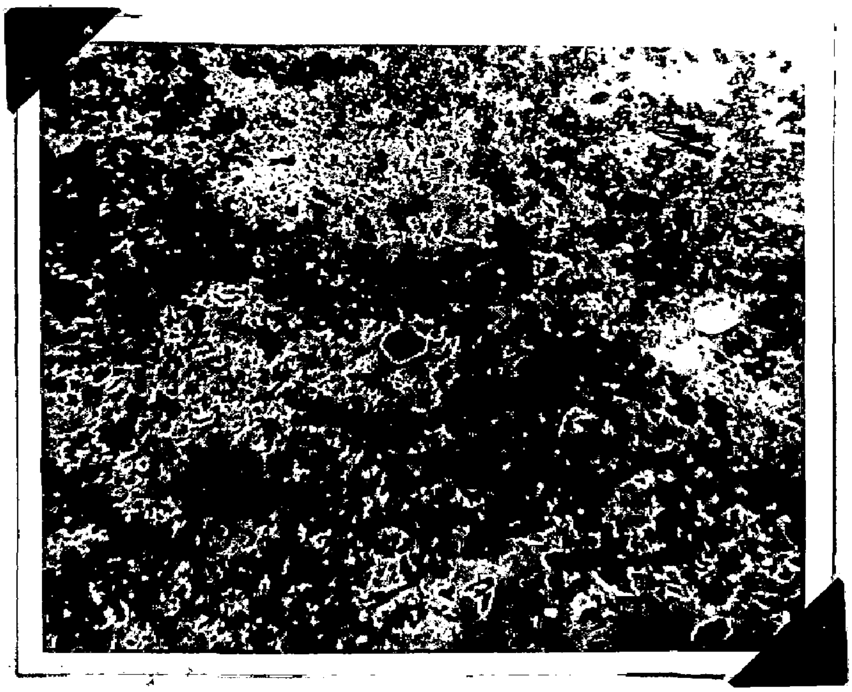
A x 160



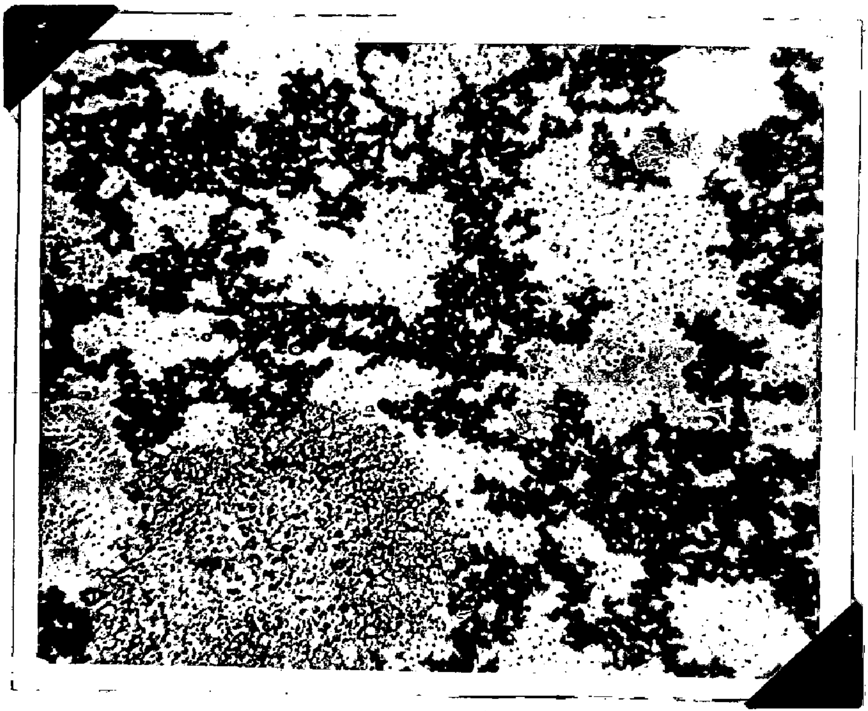
B x 160

FIG.38- REFLECTION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 103 Å THICK BARIUM STEARATE FILM TAKEN AT

(A) 77°K and (B) 291°K



A x 160



B x 160

FIG.39- REFLECTION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 515 Å THICK BARIUM STEARATE FILM TAKEN AT

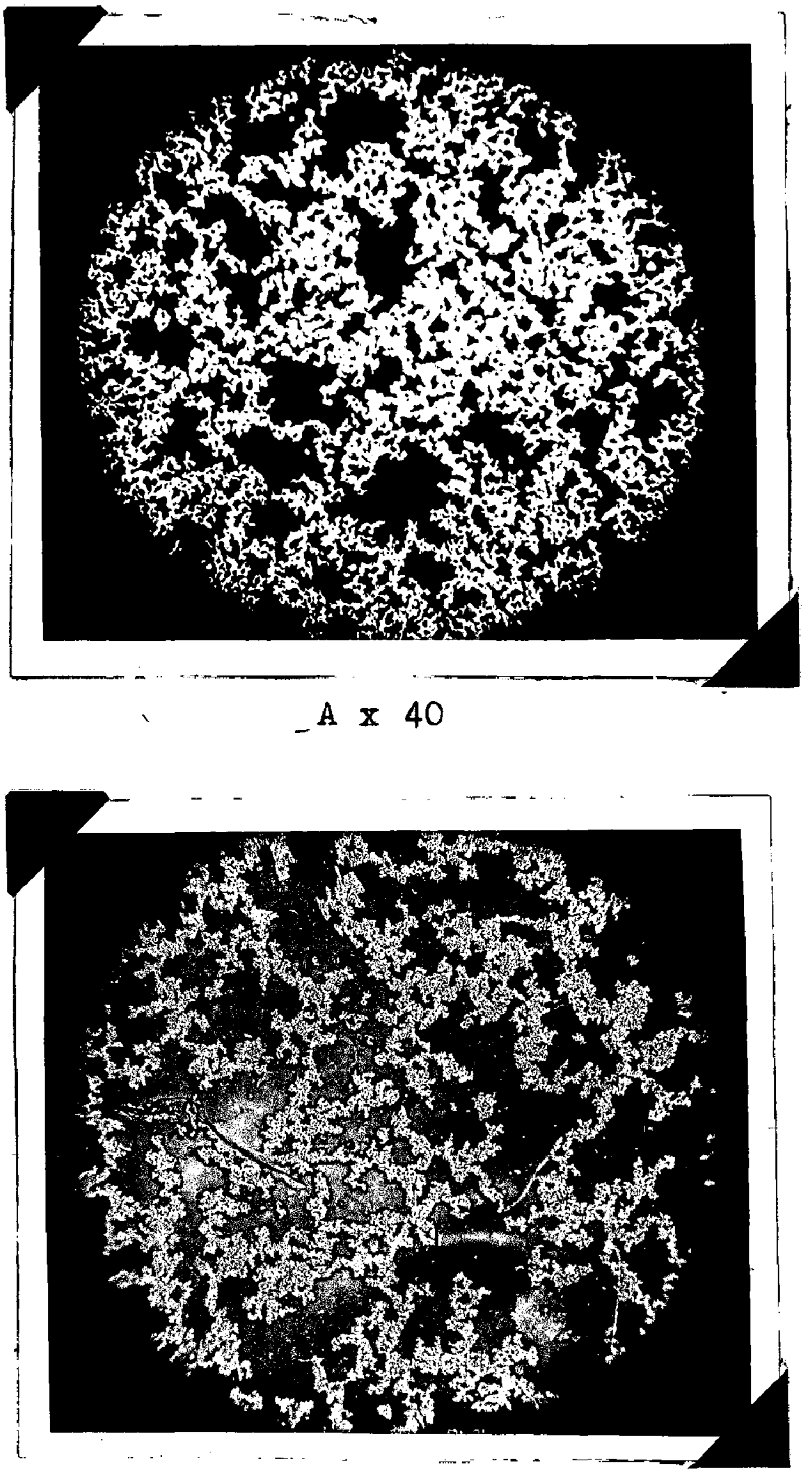
(A) 77°K and (B) 291°K

temperatures(44,113), they thus proposed that breakdown in thin specimens occurs by an avalanche initiated by tunnel emission of electrons at the cathode into the conduction band of the dielectric. Breakdown field is found independent of temperature and is a power dependent function of film thickness varying as $\omega^{-\alpha}$ where $\alpha = 0.5$ for high energy gap dielectrics(40) and for not very large electron affinity (ω is the thickness of the dielectric). This relation fits very well in our film system and the value of α is found to be very nearly equal to 0.5 in all the four substances(51,52). Measurements of the breakdown field on the present 'built-up' film system in the temperature region, below about 200°K, are in perfect accord with the above theoretically predicted temperature independence of the breakdown field (figures 16 to 19). As the highly insulating films of barium palmitate etc., presumably, have high energy gap and the electron affinity involved is not very large, presently observed results seem to be in very good agreement with Forlani-Minnaja theory. One of the basic assumptions of the F-M theory that the film be an ionic crystal is also justified in the case of 'built-up' films studied. Since the soaps or metal salts of long chain fatty acids are ionic substances (232) forming stable insoluble monolayers, 'built-up' films of barium palmitate, margarate, stearate and behenate must indeed form an ionic crystal.

At higher temperatures (above about 280°K), the electron injection is found to be governed by Schottky mechanism rather than by tunnel effect. In this case, thermionic emission of electrons takes place and the breakdown field decreases with increase in temperature due to the dominant role of electron image force on the shape of the potential barrier. The breakdown field varies with temperature in accordance with the relation

$$F \simeq \frac{\phi_{eff}}{kT} \frac{\bar{E}}{q} \frac{1}{\omega}$$

where ϕ_{eff} is the effective height of the barrier at the metal-insulator interface, $\bar{E}$ is the difference between the mean energy of the electrons able to ionize the dielectric and the mean energy of the electrons emitted from the event, k,q and ω are the Boltzman's constant, electronic charge and thickness of the insulator respectively. Theoretical curves of the breakdown field as a function of temperature (above about 200°K) have been plotted using this relation (figures 16-19). The value of ($\bar{E}$) **was** determined using the temperature independent formula of tunnel dominated breakdown(44) and is used here since the value of ($\bar{E}$) is not known for the film system studied. This procedure is justified because in these very film systems the tunnel emission dominated breakdown has already been established in the appropriate range(51,52). As can be seen from figures 16 to 19, the above relation is found to hold good in the present case. Thickness dependence data (54) of breakdown field on the present film system which provided the first

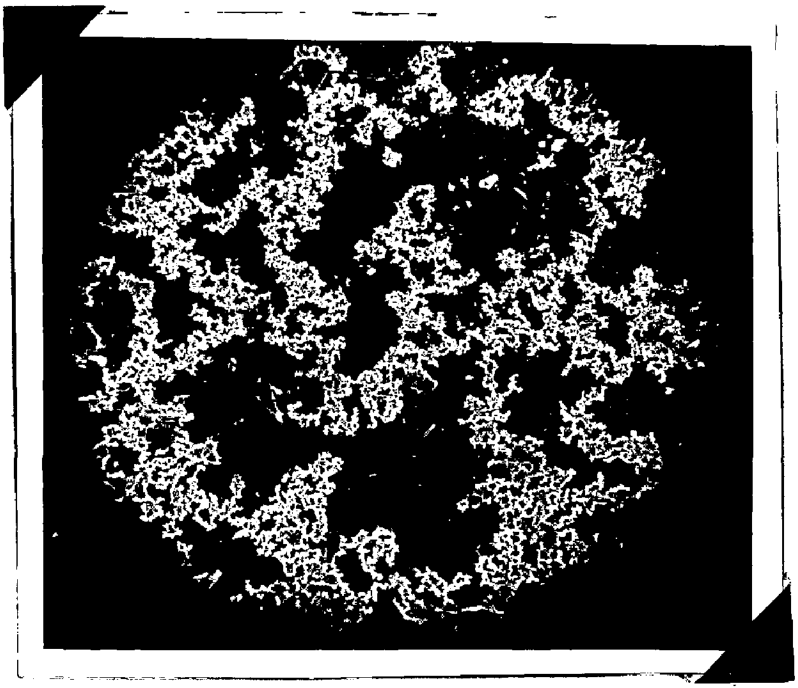


A x 40

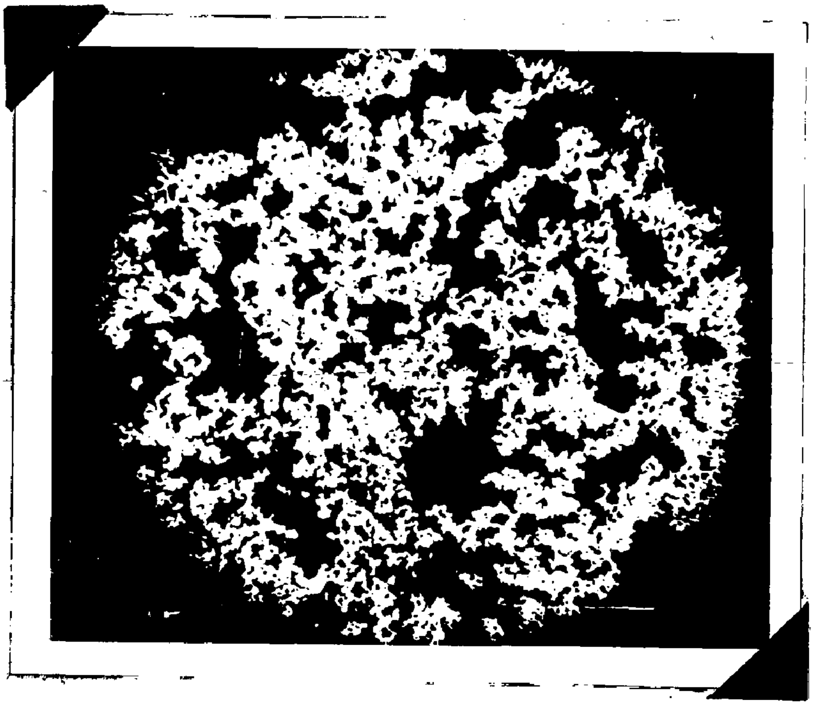
B x 40

FIG.40- TRANSMISSION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 120.2 Å THICK BARIUM BEHENATE FILM TAKEN AT

(A) 77°K and (B) 291°K



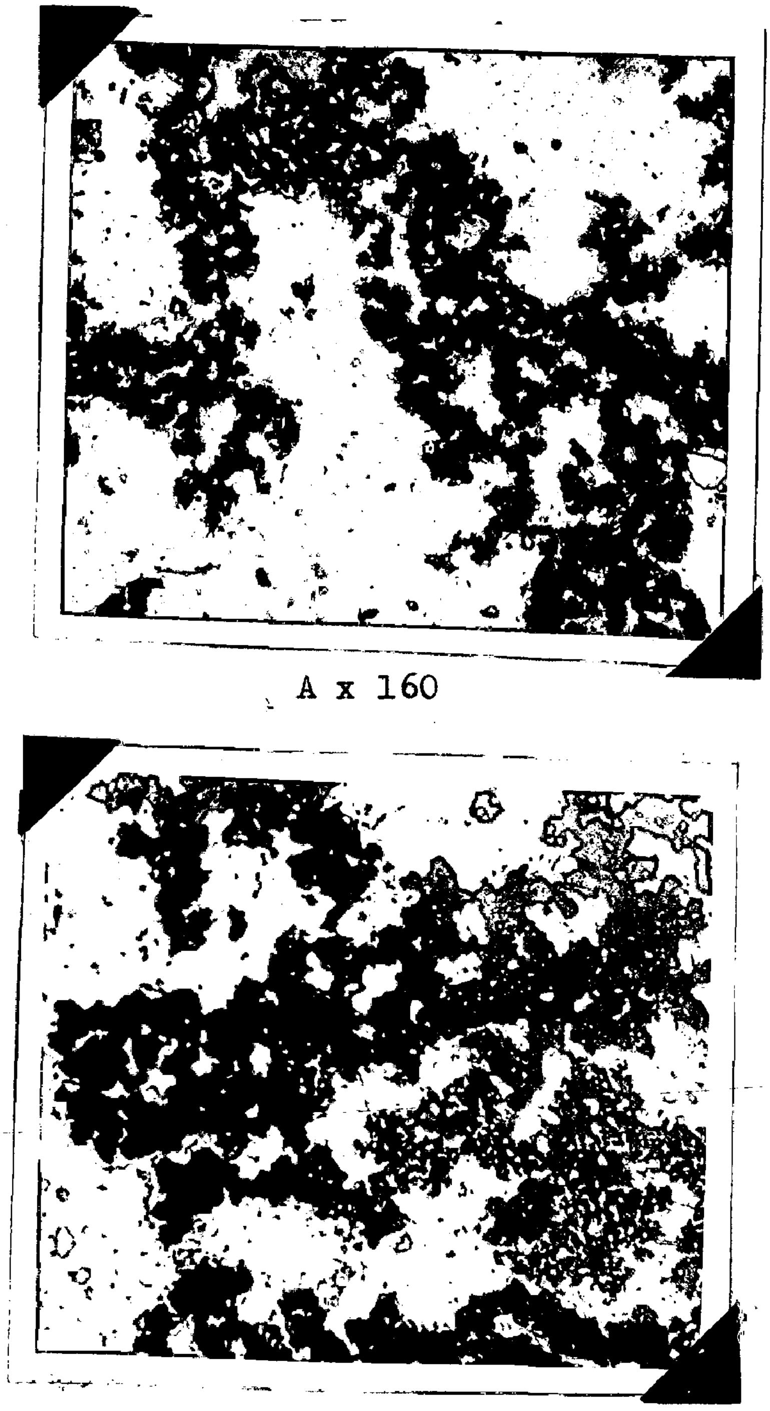
A x 40



B x 40

FIG.41- TRANSMISSION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 601 Å THICK BARIUM BEHENATE FILM TAKEN AT

(A) 77°K and (B) 291°K

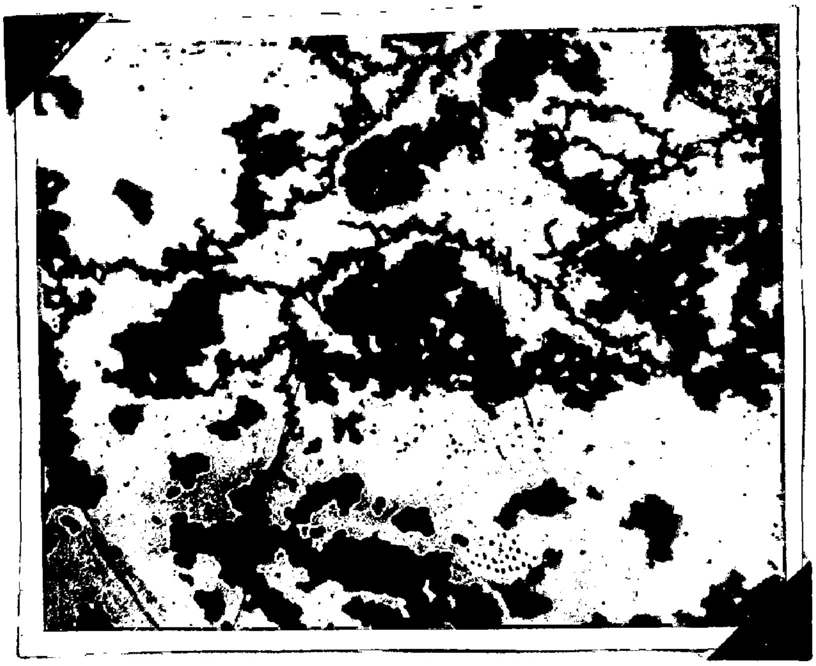


A x 160

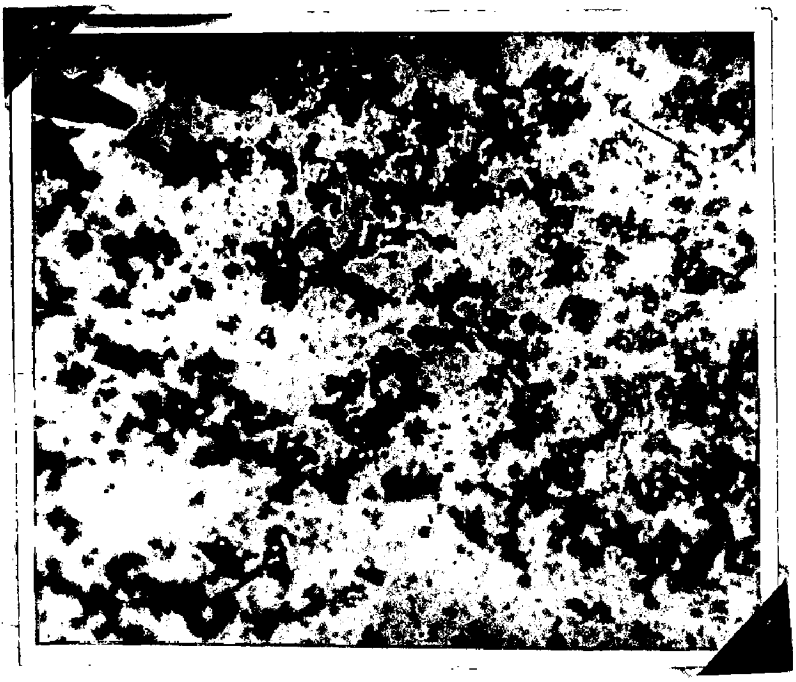
B x 160

FIG.42- REFLECTION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 120·2 Å THICK BARIUM BEHENATE FILM TAKEN AT

(A) 77°K and (B) 291°K



- A x 160



- B x 160

IG.43- REFLECTION PHOTOMICROGRAPHS SHOWING DESTRUCTION OF 601 Å THICK BARIUM BEHENATE FILM TAKEN AT

(A) 77°K and (B) 291°K

evidence for Schottky emission dominated dielectric breakdown at room temperature ($\simeq 298^\circ K$) strongly support the results obtained here.

It is thus clear from above that there should be some intermediate temperature range in which both processes i.e. tunnel as well as Schottky emission(thermionic emission) should become effective. In such a temperature range, the breakdown field is, therefore, expected to decrease slowly with increase in temperature. Our experimental data (figures 16 to 19) strongly support the above expectation in the temperature range above about $200^\circ K$ upto $280^\circ K$. Because of the commencement of the Schottky effect also in this temperature range, the breakdown field is expected to decrease as observed. A quantitative interpretation of the present data in the intermediate temperature range ($200^\circ K$ to $280^\circ K$) in which both the tunnel as well as Schottky emission play their role could not be given because the corresponding formulation in this range could not be obtained.

Handy and Scala(132) in their pioneering work on prebreakdown conduction in the present film system(metal stearates) have also found the temperature independence of the current through the film (at a fixed voltage) below about $175^\circ K$. This constancy of the current with temperature was attributed by them to be due to the conduction of electrons being dominated by tunneling at low temperatures. In the temperature range of about 175^{o}K to 315^{o}K they found the current to increase with increase in temperature. This they attributed to the conduction being governed by both tunneling as well as thermionic emission. Thus the results on temperature dependence of breakdown field studied here are consistent with those of Handy and Scala. The above discussion incidently, shows that the breakdown observed in the present film system is electronic in nature.

The maximum voltage breakdown, most commonly termed as the destructive breakdown voltage (V_{db}), which determines the 'practical ultimate dielectric strength' of the dielectric used for preparing the films (barium palmitate, stearate etc.) has also been studied here as a function of temperature. The destructive breakdown event, in our film system, is accompanied by light emission starting at the cathode just prior to the voltage collapse as was observed by Cooper and Elliot(67) in alkali halides.These authors have ascribed the light emission to the recombination processes of carriers produced by impact ionization indicating that breakdown starts by avalanching. This also shows that the breakdown presently observed is essentially electronic in nature.

Klein and his coworkers (2) classified in detail the destructive breakdown in self-healing Al-SiO-Al film systems as single holes, propagating and maximum voltage.

They regarded the first two types, to be due to the localised flaws or "weak spots" in the dielectric destroying a small area (hole type) and large area (propagating type) of the dielectric and the third one was attributed to the characteristic of the ultimate dielectric strength of the bulk material. Using small area capacitors (0.02-0.2 cm^2) they found that whole of the capacitor gets destroyed at their maximum breakdown voltage.In their study, the tests were made using d.c. voltage which was slowly increased until an isolated breakdown occured and repeated it several times till the negative resistance region in their current-voltage characteristics was attained. The mechanism in their work is that on applying electric stress across the capacitor, the leakage current rises because the capacitor can sustrain a higher voltage and the heating thus occured, destroys the whole capacitor.

Budenstein and coworkers(48,50) also studied the destructive breakdown phenomena in a variety of evaporated thin film systems. Using a different procedure from that of Klein et al. they have drawn some different conclusion in their studies on Al-SiO-Al capacitors. They employed large area capacitors (0.33-0.72 cm^2) and used a silicon-controlled rectifier (SCR) circuit enabling them in terminating the applied voltage after each breakdown. The slowly increasing voltages were applied to remove the 'weak spots' by single hole breakdown events and found that the voltage dropped at the threshold voltage when breakdown finally occured.They found that this breakdown event was indistinguishable from any other single hole breakdown in appearance or waveform etc. They also showed that whole of the capacitor area does not get destroyed even at this maximum breakdown voltage. This is also confirmed from the photomicrographs taken on the present film system (fig.28 to 43). These authors have further showed that the breakdown did not necessarily occur in the hottest part of the specimen and the entire process could be repeated in which breakdowns could sometime occur at voltages smaller than those at the previous 'weak spots'.

As the results of their experimental observations, Budenstein and Hayes(130) have concluded that Klein's 'maximum voltage breakdown' is not a basic phenomena but can be regarded as a limitation in a particular circuital context. They believe that only one form of dielectric breakdown, the 'single hole breakdown' is responsible for the destruction of the capacitor. The above referred classification of the destructive breakdown, as proposed by Klein and his coworkers was supposed to be purely phenomenological and the 'maximum voltage breakdown' was not characteristic of the bulk dielectric. According to them, the mechanism is that the breakdowns are initiated as a single hole breakdown and the total destruction occurs through a series of consecutive and many single breakdown events each of these being localised.

The film capacitors of the type Al-film-Al having thin aluminium electrodes and comparatively large areas have been employed in the present work. The 'built-up' films of long chain compounds e.g. barium stearate etc. studied here possess high structural perfection(225). These films can therefore be regarded as free from 'gross defects'(225) and 'weak spots' unlike the evaporated film systems have. When a slowly increasing d.c. voltage is applied across the film capacitor, non-shorting self-healing breakdowns occur. At the threshold of 'onset breakdown voltage', the breakdown perhaps evaporates a hole through the dielectric and an equal or larger hole through one of the electrodes only. This event is not observable in the microscope in transmission as the hole may be evaporated in one of the electrodes only and thus the film remains quite opaque not to pass light through it. When the electric stress is further increased, the current slowly increases till the destruction of the film is started. On slightly increasing the applied voltage (beyond the voltage at which the destruction in the film just commences) it was observed that the voltage collapsed and the film considerably gets destroyed over large areas due to sparks at a certain 'maximum breakdown voltage'. The whole capacitor area does not get destroyed as is clear from the photomicrographs(fig.28-43).

If required, large scale destruction of the film can, however, be avoided by simply cutting-off the supply voltage within a few microseconds of breakdown.

The 'maximum breakdown voltage' observed here is not the same and to be distinguished from the 'maximum voltage breakdown' observed by Klein and coworkers. The 'maximum voltage breakdown' of Klein and Gafni(2) was based on the appearance of the bendover in the J-V characteristics (rather than on the voltage at which destruction occurs) which they assumed to be an indication of impending breakdown. Budenstein and Hayes(48,50,130) **later** pointed out that the bendover is essentially independent of the occurrence of destructive breakdown (in capacitors of large areas) which can be attributed to regions where there is considerable heating. As the whole area of the capacitor is not destroyed in the case of present film system, even at this 'maximum or destructive breakdown voltage', it differs basically from that of Klein and Gafni. It determines the 'ultimate dielectric strength' of the dielectric for all 'practical' purposes from the point of view of device applications but is not the characteristic of the bulk as stated by Klein et al. 'Single hole' and 'propagating' breakdowns of the type Klein et al have observed **in their** work, are also not observed in the present temperature dependent studies as the film system under study was free from gross defects or weak spots unlike those in evaporated film systems. This fact seems to be supported by Budenstein et al who have considered that the breakdown observed is not necessarily due to the weak spots in the film. As the modern theories of electronic breakdown, referred to earlier, do not describe the actual mechanism of destruction, no attempt has been made to give a more detailed interpretation of the above results on destructive breakdown. Also, since these theories do not include the conduction mechanism after the onset of breakdown (in the post breakdown region), the current-voltage characteristics in the nondestructive phase could not be interpreted. However, all the results shown here, may prove useful in the device applications of the 'built-up' films which have already been shown to be promising from this point of view (132,136,223,224).

The next chapter presents the results and discussion of the temperature and frequency dependence studies of a.c. breakdown field in 'built-up' molecular Langmuir film systems.

TABLE-I

MOLECULAR PARAMETERS OF FATTY ACID SOAP MULTILAYERS

General Formula $[CH_3(CH_2)_{n-2}COO]_2$ Ba.

Substance	Molecular Formula	No. of carbon atoms in hydro-carbon chain	Value of mono-layer thick-ness (Å)	Melting point °C⊠⊠	Type of the film	Type of solution used for deposition	pH of the solution	Dielectric constant of the monlayer film+	Dielectric constant of multi-layer film+	Electronic polarizability of the molecule x10-24CC≠
Ba-Palmitate	$[C_{15}H_{31}COO]_2Ba$	16	23.25	63	Y	$3x10^{-5}M$ $BaCl_2$ $4x10^{-4}M$ $KHCO_3$	7-7.2	1.67	2.85	107.68
Ba-Margarate	$[C_{16}H_{33}COO]_2Ba$	17	24.05	60	Y	"	7-7.2	1.65	2.59	111.36
Ba-Stearate	$[C_{17}H_{35}COO]_2Ba$	18	25.75	70	Y	"	7-7.2	1.62	2.72	115.04
Ba-Behenate	$[C_{21}H_{43}COO]_2Ba$	22	30.05	80	Y	"	7-7.2	1.60	2.25	129.76

⊠ Reference 203 + Reference 137

⊠⊠ Reference 155 ≠ Reference 137

TABLE-II

TEMPERATURE DEPENDENCE (BETWEEN 77°K AND 320°K) OF D.C.'ONSET' BREAKDOWN FIELD DATA

Fig No.	Substance	Thickness range studied (Å)	'Onset' breakdown voltage (V_b) in volts				'Onset' breakdown field (F_b) in MV/cm			
			for 2 layers	for 4 layers	for 8 layers	for 20 layers	for 2 layers	for 4 layers	for 8 layers	for 20 layers
16	Ba-Palmitate	46.5- 465.0	3.35- 2.9	4.1- 3.53	4.0- 2.98	4.47- 3.53	7.20- 6.20	4.40- 3.80	2.15- 1.60	0.96- 0.76
17	Ba-Margarate	48.1- 481.0	3.46- 3.175	3.85- 3.37	3.85- 2.7	4.33- 3.85	7.20- 6.60	4.0- 3.50	2.00- 1.40	0.90- 0.80
18	Ba-Stearate	51.5- 515.0	4.38- 3.15	4.02- 3.14	3.91- 3.3	4.635- 3.86	8.50- 6.10	3.90- 3.05	1.90- 1.60	0.90- 0.75
19	Ba-Behenate	60.1- 601.0	4.27 3.70	4.33- 3.6	4.09- 3.1	4.51- 2.52	7.10- 6.16	3.60- 3.00	1.70- 1.30	0.75- 0.42

TABLE-III

CURRENT-VOLTAGE CHARACTERISTICS OF 'BUILT-UP' FILMS

Fig. No.	Substance	Curve No.	No. of layers	Thickness of the film in Å	Temperature of the film in ^{o}K	Capacitor Area in cms.sq.	Onset break-down voltage (V_b) in volts
20	Barium Palmitate	A	4	93.0	77	0.430	4.50
		B			291	0.390	3.85
		C			291	0.400	3.90
		D	20	465.0	77	0.420	4.70
		E			291	0.430	4.30
		F			291	0.430	4.60
21	Barium Margarate	A	4	96.2	77	0.400	3.70
		B			291	0.400	3.50
		C			291	0.430	2.80
		D	20	481.0	77	0.410	4.20
		E			291	0.430	3.15
		F			291	0.390	3.25
22	Barium Stearate	A	4	103.0	77	0.425	3.90
		B			291	0.410	3.40
		C			291	0.420	3.80
		D	20	515.0	77	0.415	4.00
		E			291	0.410	3.50
		F			291	0.385	4.20
23	Barium Behenate	A	4	120.2	77	0.430	4.00
		B			291	0.415	3.10
		C			291	0.420	3.30
		D	20	601.0	77	0.420	4.40
		E			291	0.410	3.50
		F			291	0.435	3.80

TABLE-IV

TEMPERATURE DEPENDENCE (BETWEEN 77°K AND 320°K) OF D.C. 'DESTRUCTIVE' BREAKDOWN FIELD DATA

Fig. No.	Substance	Thickness range studied in Å	Destructive Breakdown Voltage (V_{db}) in volts				Destructive Breakdown Field (F_{db}) in 10^7 V/cm			
			for 2 layers	for 4 layers	for 8 layers	for 20 layers	for 2 layers	for 4 layers	for 8 layers	for 20 layers
24	Ba-Palmitate	46.5- 465.0	87.2- 73.25	91.00- 74.5	96.7- 79.0	90.00- 42.0	18.75- 15.75	9.80- 8.0	5.20- 4.25	1.940- 0.900
25	Ba-Margarate	48.1- 481.0	87.5- 80.50	96.20- 87.5	96.2- 75.0	90.19- 43.3	18.20- 16.70	10.00- 9.1	5.00- 3.90	1.875- 0.900
26	Ba-Stearate	51.5- 515.0	91.5- 77.25	88.58- 78.28	87.5- 80.0	88.84- 42.5	17.75- 15.00	8.60- 7.60	4.25- 3.90	1.725- 0.825
27	Ba-Behenate	60.1- 601.0	88.4- 79.60	91.59- 79.93	89.0- 77.0	84.15- 3.61	14.70- 13.25	7.62- 6.65	3.70- 3.20	1.400- 0.600

TABLE-V

DETAILS OF PHOTOMICROGRAPHS

Fig. No.	Substance	No. of layers	Thickness of the film in Å	Technique of photography used	Capacitor Area in cms.sq.		Applied Voltage (V_{db}) volts	
					A	B	A	B
28	Barium Palmitate	4	93.0	Transmitted	0.430	0.410	86.0	76.80
29		20	465.0	Transmitted	0.395	0.415	83.5	70.00
30		4	93.0	Reflected	0.450	0.490	86.0	76.80
31		20	465.0	Reflected	0.410	0.420	83.5	70.00
32	Barium Margarate	4	96.2	Transmitted	0.425	0.410	96.0	87.60
33		20	481.0	Transmitted	0.470	0.445	88.0	74.50
34		4	96.2	Reflected	0.430	0.440	96.0	87.60
35		20	481.0	Reflected	0.460	0.450	88.0	74.50
36	Barium Stearate	4	103.0	Transmitted	0.400	0.400	86.0	86.00
37		20	515.0	Transmitted	0.370	0.400	76.8	74.20
38		4	103.0	Reflected	0.430	0.420	86.0	86.00
39		20	515.0	Reflected	0.440	0.410	76.8	74.20
40	Barium Behenate	4	120.0	Transmitted	0.420	0.430	88.0	80.38
41		20	601.0	Transmitted	0.410	0.420	80.0	71.40
42		4	120.2	Reflected	0.400	0.420	88.0	80.38
43		20	601.0	Reflected	0.420	0.415	80.0	71.41

(1) All the transmission and reflection photomicrographs marked 'A' are the photographs of the films destructed at 77^{o}K and that marked 'B' are at 291^{o}K.

(2) All the transmission photomicrographs are forty times magnified (x40) and all the reflection photomicrographs are ohe hundred sixty times magnified (x160).

CHAPTER-VII

RESULTS ON A.C. BREAKDOWN AND DISCUSSION

As has been stated earlier, 'built-up' films of metallic salts of some long chain fatty acids(e.g. barium palmitate, stearate etc.) have recently been shown to be promising for making some miniaturised solid state dielectric devices (132,136,223,224) like tunneling sandwich between superconductors etc. First detailed and systematic study of the d.c. breakdown characteristics of such 'built-up' dielectric films have been done by the author as reported in the preceding chapters (Chapter V and VI). The a.c. breakdown characteristics of present film systems are known to be equally important from the point of view of device applications and particularly interesting is the first i.e. the 'onset' breakdown event in these films. Only few efforts to investigate the breakdown field with alternating voltages have been done by the pioneering workers of this interesting field and the only a.c. studies reported in the literature are by Anno(233), Chaiken and St.John(234) and by Klein and Levanon(125). Thickness and frequency dependence of a.c. breakdown field (at room temperature) in'built-up' films have been reported by Agarwal and Srivastava(122).Anno has taken his measurements on mineral films whereas Klein and Levanon have investigated thermally evaporated silicon monoxide films sandwiched between two aluminium electrodes. Even in the studies of these authors, no systematic temperature dependence of breakdown field has been reported which, obviously, is important from the device application point of view. As the temperature in most of the devices plays an important role, the present temperature dependent investigations in 'built-up' film systems might have proved very useful for this purpose.These films have already been shown very suitable for carrying out present investigations (Chapter V). This chapter describes the results of a detailed study of the temperature and frequency dependence of a.c. 'onset' breakdown field in 'built-up' films of barium palmitate, margarate, stearate and behenate and the possible interpretation of the results is also discussed.

7.1 RESULTS

Measurements of the breakdown field in 'built-up' thin films of the metal salts of fatty acids e.g. barium palmitate, margarate, stearate and behenate have been carried out under alternating field conditions as a function of temperature in the range from liquid nitrogen temperatures to well above the room temperature ($320^{o}K$) at a fixed frequency (30 KHz) and for four layers and 20 layers thick films. The measurements were also taken for varying frequencies in the range from 10 KHz to 100 KHz at two fixed temperatures, $77^{o}K$ and $290^{o}K$ for two thicknesses

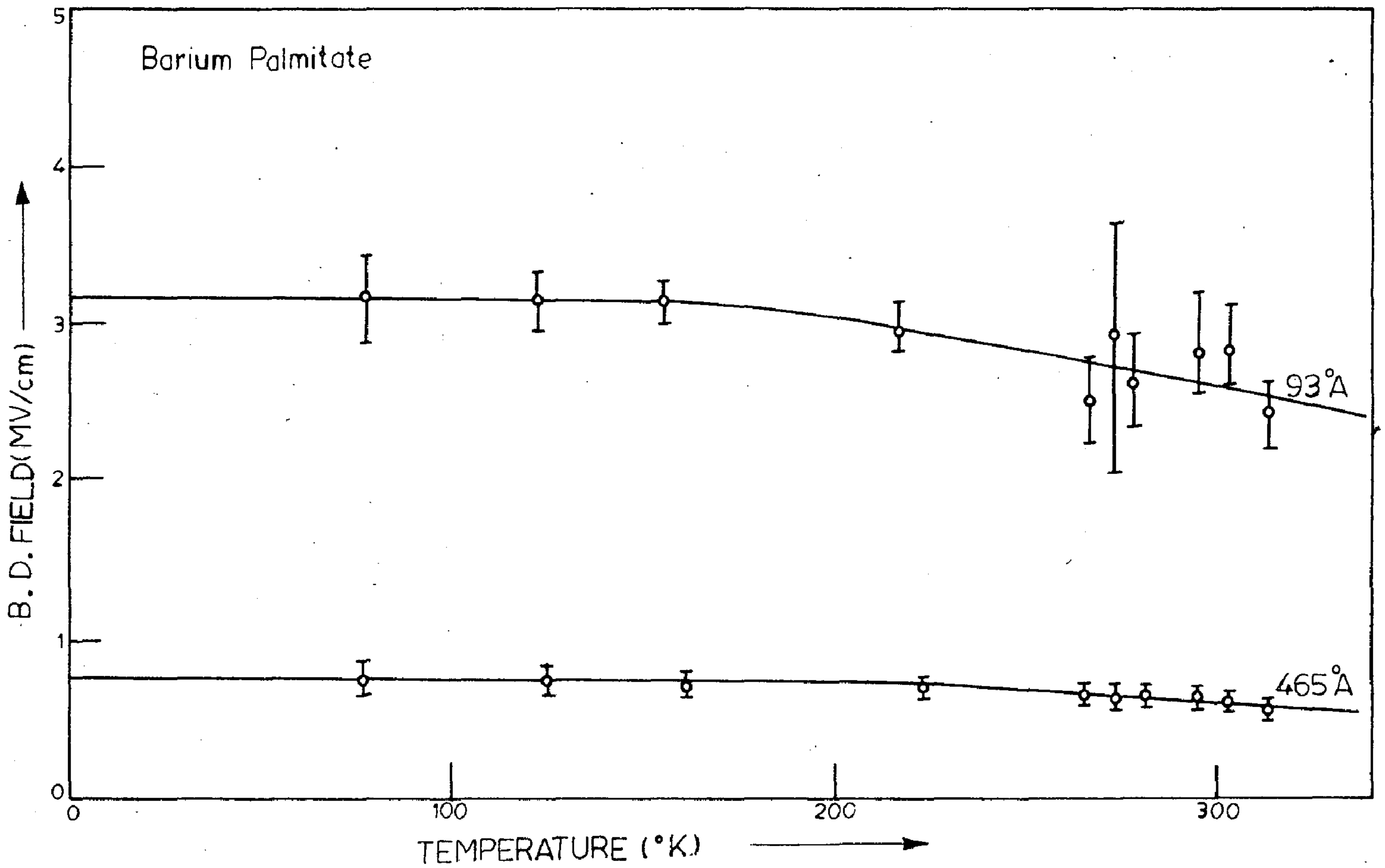


FIG.44 - Temperature v/s A.C. breakdown field at a fixed frequency, 30 KHz.

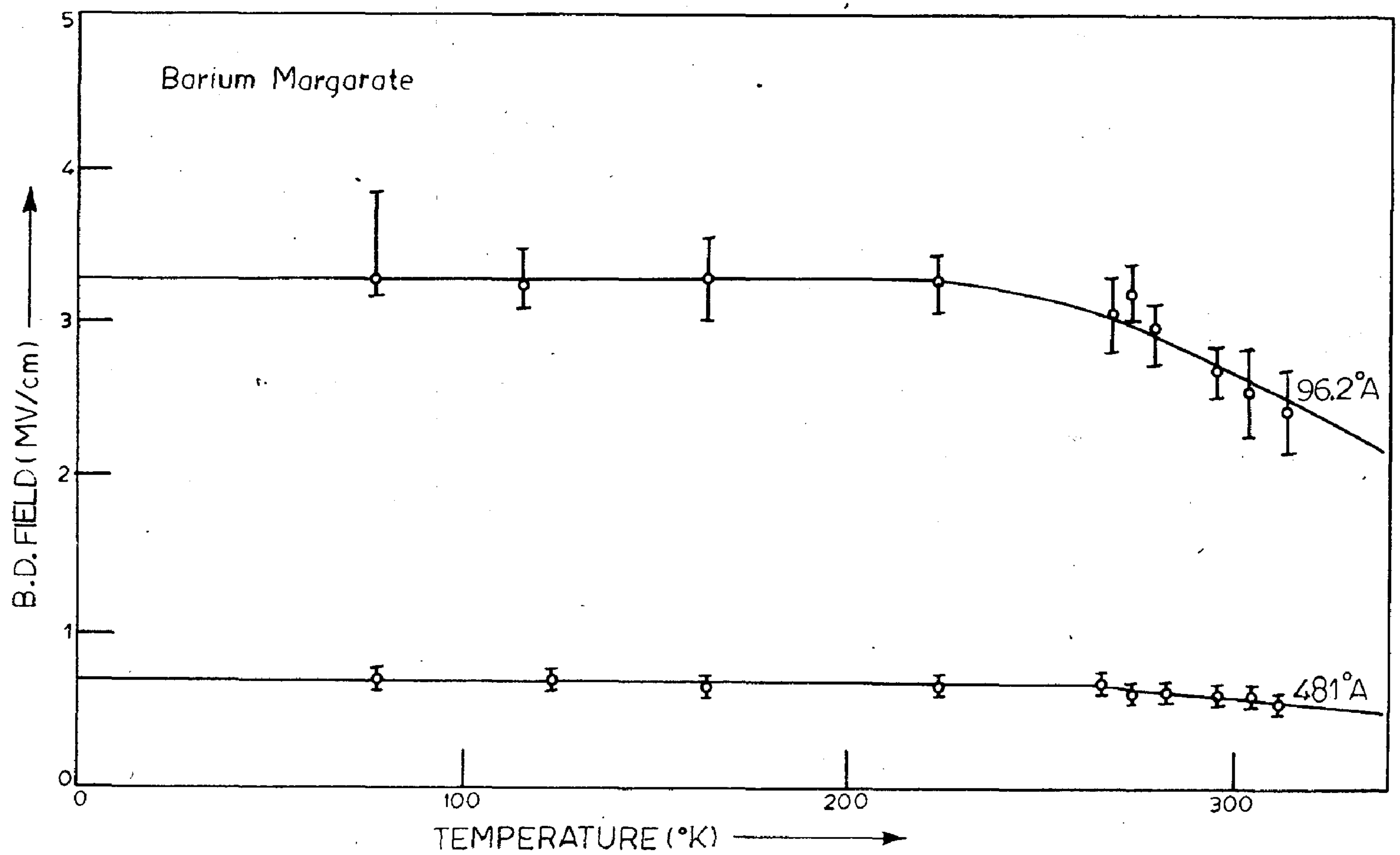


FIG.45 - Temperature v/s A.C. breakdown field at a fixed frequency, 30 KHz.

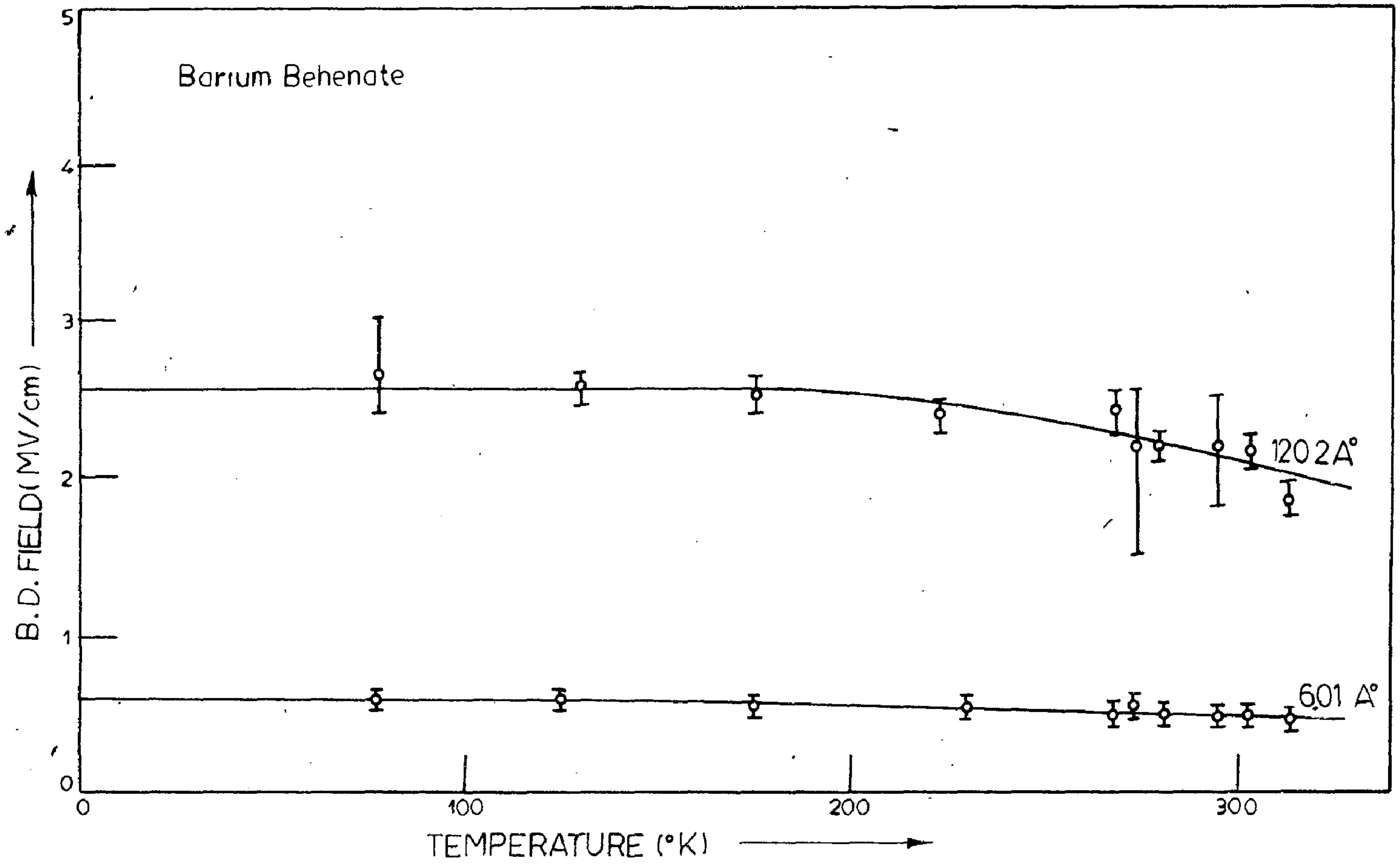


FIG.46 _ Temperature v/s A.C. breakdown field at a fixed frequency, 30 KHz.

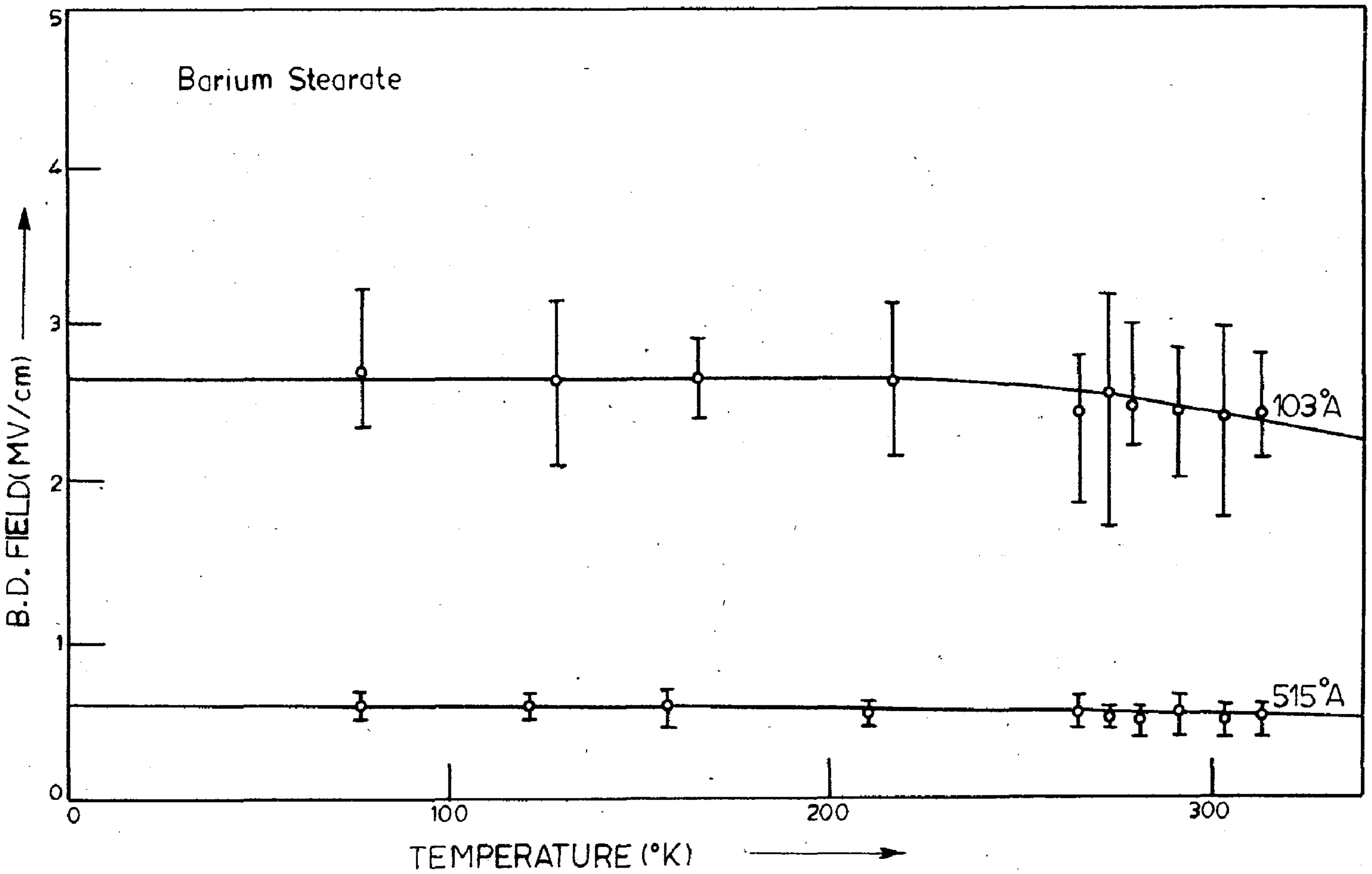
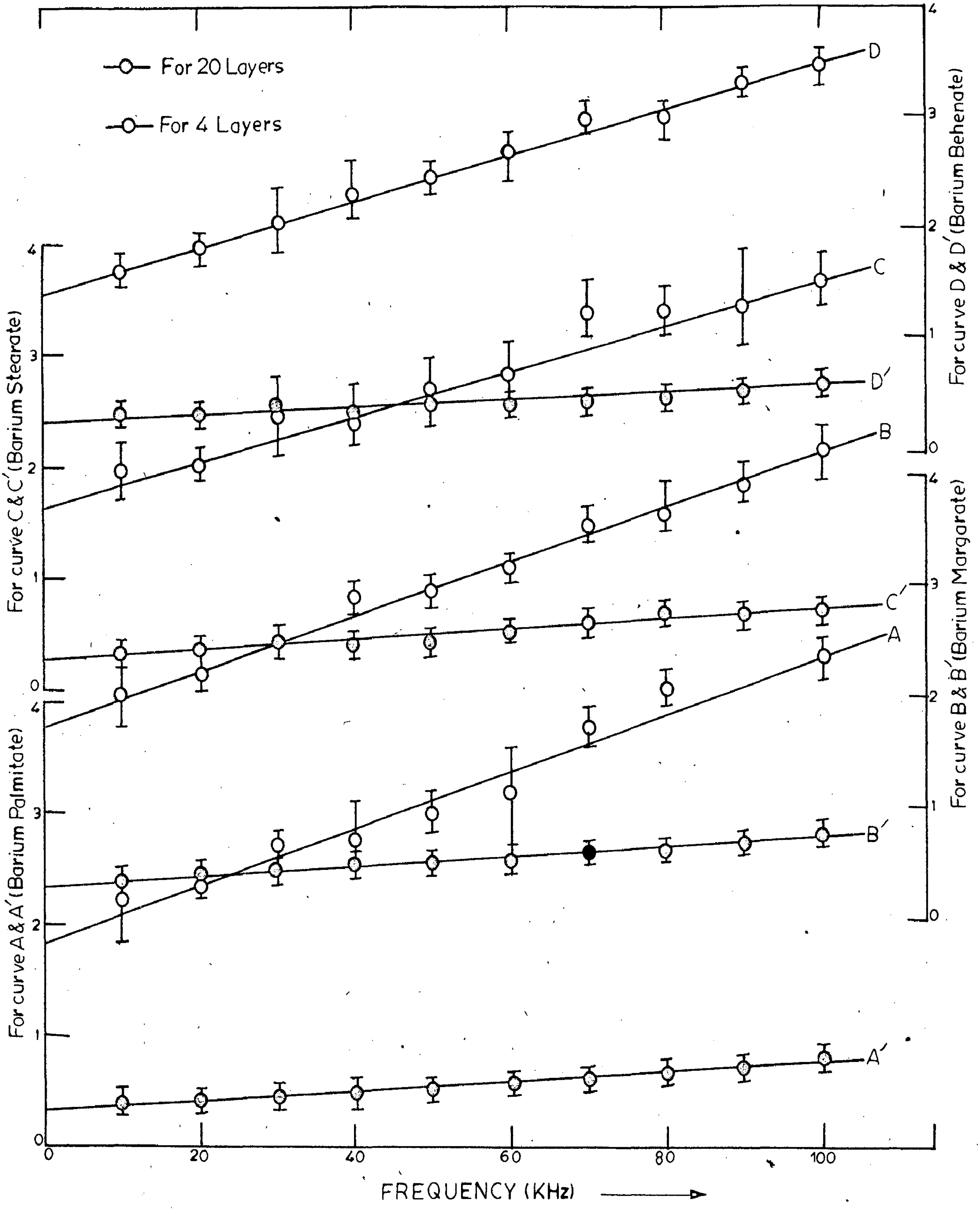


FIG.47 Temperature v/s A.C. breakdown field at a fixed frequency, 30 KHz.

of the films (4 and 20 layers).

The sandwich structure of the type Al-film-Al with 4 layers and 20 layers thick films were fabricated with the technique as described earlier in the Chapter V. The breakdown field (which is the ratio of the breakdown voltage to the thickness of the film)was measured using the circuit given in Sec.5.5(b). The lebelled figures 44, 45, 46 and 47, shows graphical representation of the a.c. 'onset' breakdown field as a function of temperature and with the thickness of the film as a parameter for 'built-up' films of barium palmitate, margarate, stearate and behenate respectively. The variation of a.c. breakdown field with frequency of the applied electric stress is presented in figure 48 for all the four substances at 77°K. It is found that the breakdown field increases rapidly with frequency while a slight decrease is observed with the increase in temperature at higher temperatures (above about 200°K). All these curves have been plotted using 'best-fit' of the experimental points. The dots in the graphs correspond to the mean values of the few observations taken on similar films fabricated under identical conditions and the scatter in the experimental data has also been shown. The nature of the breakdown with a.c.voltages appeared to be similar to that of d.c., however, the a.c. breakdown voltages are found lesser than the corresponding d.c. ones. The results obtained on the temperature dependence and frequency dependence



IG.48_ Frequency (KHz) v/s A.C. breakdown field at a fixed temperature (77°K).

of the a.c. breakdown field have also been given in table VI and VII respectively.

7.2 DISCUSSION

Mainly three types of destructive breakdowns were distinguished by Klein and Levanon(125) in self-healing Al-Sio-Al film systems as was done by Klein and co-workers in their d.c. studies(2). As the 'built-up' films of some organic compounds studied here, have been reported to possess high structural perfection and to be free from gross defects(225) or 'weak spots', the results obtained on a.c. breakdown voltage, are suitable to be compared with theoretical predictions as in the d.c. studies. Here, also, one of the two general breakdown mechanisms i.e. thermal and electronic can be effective. Accidently, the frequency dependence of the breakdown strength calculated on the basis of the thermal breakdown theory (According to which the breakdown field should decrease with frequency) turns out to be opposite(125) to the one experimentally observed here showing that the breakdown observed here can not be thermal in nature. It has already been **shown** in d.c. studies (section 6.2) that the results on d.c. breakdown are best explainable with the electronic breakdown theory of Forlani and Minnaja which is based on electron ionization avalanches in ionic crystals. Therefore, it can safely be concluded that the breakdown observed here, is nonthermal and is presumably electronic in nature.

Since the theory of a.c. effects in electronic breakdown processes has not yet been explicitly formulated, the observed frequency and temperature dependence of the a.c. dielectric breakdown field could not be interpreted in greater detail. However, the results may prove useful in the a.c. device applications of the 'built-up' Langmuir films, involving self-healing, non-shorting capacitor systems.

The next and the last chapter describes the concluding remarks on the studies reported on 'breakdown field measurements'. A summary of the results with their importance for the subject and electronic technology is given. Some suggestions for the possible work which may be carried in future have also been given.

TABLE-VI

TEMPERATURE DEPENDENCE (FROM 77°K TO 320°K) OF A.C. BREAK-DOWN FIELD AT 30 KHz

Fig. No.	Substance	Thickness range studied in (Å)	Breakdown Voltage in Volts		Breakdown field in 10^6 Volts/cm	
			for 4 layers	for 20 layers	for 4 layers	for 20 layers
44	Ba-Palmitate	93.0-465.0	2.96-2.140	3.45-2.930	3.18-2.30	0.74-0.63
45	Ba-Margarate	96.2-481.0	3.35-2.165	3.51-2.840	3.48-2.25	0.73-0.59
46	Ba-Stearate	103.0-515.0	2.90-2.470	3.14-2.575	2.80-2.40	0.61-0.50
47	Ba-Behenate	120.2-601.0	3.245-2.520	3.61-2.880	2.70-2.10	0.60-0.48

TABLE-VII

FREQUENCY DEPENDENCE (10 TO 100 KC/SEC) OF BREAKDOWN FIELD AT 77°K (FIG.48)

Substance	Thickness range studied (Å)	Breakdown voltage in Volts		Breakdown field in volts/cm.	
		For 4 layers	For 20 layers	For 4 layers	For 20 layers
Ba-Palmitate	93.0-465.0	1.72-4.14	1.21-3.120	1.85-4.45	0.260-0.67
Ba-Margarate	96.2-481.0	1.92-4.04	1.635-3.175	2.00-4.20	0.340-0.66
Ba-Stearate	103.0-515.0	1.90-3.81	1.185-3.140	1.85-3.70	0.23-0.61
Ba-Behenate	120.2-601.0	1.95-4.21	2.01-3.065	1.62-3.50	0.335-0.51

CHAPTER-VIII

CONCLUSIONS

8.1 SUMMARY OF THE RESULTS

Since the mechanism of dielectric breakdown in thin insulator films is little understood, it is therefore, is a subject of many theoretical and experimental investigations. Owing their use in making and developing thin film solid state devices like thin film capacitors, tunneling sandwich structures etc., all the data presented in this dissertation may prove important. The purpose of the present study was to show the suitability of the 'built-up' thin films of long chain fatty acids for the fabrication of high dielectric strength, high value capacitors and to relate the conditions such as temperature, with the breakdown events. The results given here provide new evidence in support of Forlani-Minnaja's electronic breakdown theory.

The capacitor structures of the type Al-Film-Al were fabricated using 'built-up' Langmuir films of metallic salts of some long chain fatty acids (e.g. barium palmitate, margarate, stearate and behenate) as the insulating media between two thermally deposited aluminium films of nearly constant thickness under high vacuum with the help of a 6" coating unit suitable for this purpose. Insulating films were built-up by a delicate but easy technique of Blodgett and Langmuir(61,62) from which even the films of molecular thicknesses can be built-up by transferring them from the highly cleaned water surface under a constant surface pressure. These films are found very suitable for the present studies carried out because their thicknesses are closely controllable in low ranges and are accurately known(202, 203). Structurally these Langmuir films have been reported to be free from gross defects(225) and weak spots (unlike the case with the dielectric films deposited by the thermal evaporation technique) forming hexagonal crystals with the symmetry axis (optic axis) perpendicular to the plane of the film(182).These films have also been found to possess some additional advantages like high dielectric strength, uniformity, reproducibility and good thermal stability which, of course, was necessary for the investigations carried out by the author. The thermal evaporation does not cause any change in the deposited film(121).

It is shown that when a film insulator is used between two thin metal electrodes, a high breakdown strength of the system is observed. A detailed and systematic study of the temperature dependence of the breakdown field has been carried out by the author in the most workable and useful temperature range for the devices from well above the room temperature ($313^{o}K$)

down to liquid nitrogen temperatures (77°K). Two breakdown events widely different from each other were observed, one for the 'onset' of breakdown (V_b) at which the current through the insulator shoots-up suddenly from its low values and the other 'maximum breakdown voltage' at which a large area of the insulator film gets destroyed and is also termed as destructive breakdown voltage (V_{db}). Both the breakdown events were studied using linearly increasing d.c. electrical voltages applied to the capacitor. The variable temperature measurements were taken with the help of a self-designed and fabricated thermal probe which forms a part of the heat shield cryostat.

At lower temperatures, below about 200°K, the injection of the electrons from the cathode was found to be dominated by the tunnel effect and the breakdown field virtually independent of temperature. Above about 280°K, a shift in the current to higher levels is noted, indicating the existence of the Schottky barriers at the electrode-insulator interface. The breakdown field in this temperature range is found to decrease with temperature due to electron injection being governed by the Schottky emission or thermionic emission. In the intermediate temperature range (between 200°K and 280°K) both the tunnel as well as Schottky emission were found to play their role. The breakdown field in this range decreases slowly with increase in temperature in quantitative agreement with theory(44).

A comparison of the breakdown strength data with published theories showed that the best agreement was obtained with the electron ionization avalanche model as developed by Forlani and Minnaja(44). Their power dependence of the breakdown field on thickness ω ($F \propto \omega^{-0.5}$) fits the experimental data of the present film system. Their theory is based purely on field emission showing that the breakdown observed in the present case was electronic in nature. Other theories of breakdown (intrinsic, thermal etc.) are not in perfect agreement with the data observed.

A study of the 'maximum breakdown voltage' or the 'destructive breakdown voltage' was made and the destructive breakdown field vs. temperature as plotted in the figures(24-27), shows a decrease with increasing temperatures. The destruction of the film was accompanied by light emission starting at the cathode just prior to the voltage collapse as was observed by Cooper and Elliot in alkali halides indicating that the breakdown starts by avalanching. In the destructive breakdown process as whole area of the capacitor does not get destroyed even at this maximum or destructive breakdown voltage, it differs basically from that of Kleins and Gafni(2) who have classified the destructive breakdown in Al-SiO-Al film systems as 'single holes', 'propagating' and 'maximum voltage'.

As was stated by Budenstein and Hayes(48,50) in their work, the possible mechanism of destruction here also is supposed that the breakdowns are initiated as a single hole breakdown and the total destruction occurs through a series of many single, localised breakdown events and at the threshold of 'onset' breakdown, the breakdown perhaps evaporates a hole through the dielectric and an equal or larger hole in one of the electrodes only. This event was not observable in microscope as the film even after breakdown remained opaque enough not to pass light through it.

The destructive breakdown field determines the 'ultimate dielectric strength' of the dielectric for all practical purposes from the point of view of device applications but is not the characteristic of the bulk as stated by Klein et al. 'Single hole' and 'propagating' breakdowns of the type Klein et al have observed in their work are also not observed in the present temperature dependent studies (as is clear from photomicrographs) as the films were free from gross defects and weak spots. This fact is supported by the work of Budenstein et al who have considered that the breakdown observed is not necessarily due to the weak spots in the film. As the modern theories do not describe the actual mechanism of destruction, the results on destructive breakdown event are not interpreted theoretically. The photomicrographs show destruction of the film over large areas.

The variation of a.c. 'onset' breakdown field with temperature show a similar nature to that with d.c. voltages but the breakdown fields are found relatively smaller to the corresponding d.c. ones. These results could not be interpreted theoretically due to the lack of a breakdown theory for a.c. fields. The frequency dependence of a.c. breakdown field in these films show a reverse nature to that calculated with the thermal breakdown theory(125) thus showing the nonthermal nature of the breakdown events occured in the present film system.

As sometimes in the devices the requirements of temperatures are extreme, all the data presented in this dissertation may prove useful in the development of some modern solid state dielectric devices.

8.2 SCOPE FOR FURTHER INVESTIGATIONS

It is expected that in future the multilayer Langmuir films will be increasingly used for studying various basic phenomena and in thin film device appoications. In particular, the promising electronic device applications of the film having certain great advantages over those existing at present may soon be realised in practice. The multilayers will be useful in any study which involves an ultrathin dielectric film of uniform, controllable and known thicknesses.

Uptil now, the studies of the breakdown field and its dependence upon thickness and temperature in the 'built-up' films have been performed. A closer study of the effects of electrode material and various other parameters on the breakdown field also seems desirable and are suitable topic for further investigations. Such investigations may shed more light on breakdown mechanism in these films.

An improvement of the breakdown apparatus would be to make it more sophisticated using electronic switches. The most obvious suggestion, perhaps, is that the same general plan of investigations be used in a study of other dielectrics both amorphous and crystalline.

With the help of all these studies it may become possible to develop some useful dielectric devices. These might be the fabrication of high, known capacitors, thin film integrated circuit elements, tunneling devices between metals and superconductors etc. Perhaps, the most interesting and fascinating applications of 'built-up' multilayers are those involving their use as controlled 'thickness spacers' or 'distance keepers' which are useful in the photographic sensitization mechanism(235,236). Drexhage and colleagues(237) make ingenious use of monomolecular layers as probes for studying the fundamental structure and properties of light waves which have become important in the display and measurement of the width of the fascinating ultrashort (picosecond) laser pulses. Some of the applications such as those involving studies of biological processes and evaporation control etc. are also commendable.Finally, since layered structure of organic molecules play an important role in nature and in natural organic compounds like cholesterol can be used for 'building-up' suitable layer systems. These artificial crystals may provide fresh insight into some life processes. The above promising future applications of these film systems have been described in a monograph on 'built-up' molecular films and their applications' by Srivastava(236).

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APPENDIX

LIST OF PUBLICATIONS

1. Temperature Dependence of D.C. destructive Breakdown Field in 'Built-up' Barium Stearate Films.

   Solid State Communications (U.S.A.), Pergamon Press, Vol.11, No.10, p.1461(1972).

2. Temperature Dependence of Breakdown Field in Barium Stearate Multilayer Films.

   Thin Solid Films (Switzerland), Vol.14,No.2,p.367(1972).

3. On the Validity of Faucher's Ellipsometric Formulae.

   Ind. J.of Pure and Appl.Physics, Vol.11, No.2,p.137 (1973).

4. Temperature Dependence of D.C.Breakdown Field in Thin 'Built-up' Barium Palmitate Films.

   Indo-Soviet Conference, Bangalore(India), 11 to 16 Dec. 1972, (Accepted for presentation).

5. Measurement of Temperature Dependence of D.C.Breakdown Field in Thin 'Built-up' Margarate Films.

   Symposium on Solid State Materials. NPL. New Delhi(India), 6-10 Feb.1973(Accepted for presentation).

6. A Study of the Temperature Dependence of D.C.destructive Breakdown Field in Barium Palmatate Films.

   Nuclear Physics and Solid State Physics Symposium (Chandigarh), 28 Dec.1972-1st Jan., 1973 (Accepted for presentation).

7. A Study of the Breakdown Field as a Function of Temperature.

   Nuclear Physics and Solid State Physics Symposium 27th Dec.1974-31st Dec.1974(Accepted for presentation).

8. Temperature Dependence of Breakdown Field in 'Built-up' Langmuir Films.

   Thin Solid Films (Switzerland), Vol.27, No.1, p.49-62 (1975).

Solid State Communications, Vol. 11, pp. 1461–1466, 1972. Pergamon Press. Printed in Great Britain

TEMPERATURE DEPENDENCE OF d.c. DESTRUCTIVE BREAKDOWN FIELD IN 'BUILT-UP' BARIUM STEARATE FILMS

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Since the 'built-up' molecular films of barium stearate have been shown to be promising for making thin film dielectric devices, a study of their breakdown characteristics is essential. Particularly, in device applications, the range of operating voltage is very important and therefore a study of the maximum dielectric strength of the films is highly desirable. Since the devices may be required to operate at various temperatures, it is all the more necessary to investigate the temperature dependence of the maximum dielectric strength. Such a temperature dependent study of the dielectric strength of barium stearate films has been reported in the present work in the range (–40 –40°C). The dielectric strength is found to decrease with increasing temperature. Typical current–voltage characteristics with and without a series resistor and a representative transmission micrograph have also been given. The photomicrograph shows destruction of the film over large areas. As the modern theories do not describe the actual mechanism of destruction adequately, no attempt has been made to interpret the results theoretically. However, the results may prove useful in device applications of barium stearate films, involving self healing, nonshorting capacitor systems.

1. INTRODUCTION

THE DIELECTRIC breakdown studies of thin films are currently receiving widespread interest as a new area of stimulating research because of their potential usefulness for the development of passivated devices, micro-electronic and integrated circuits, field effect transistors etc. Recently, the 'built-up' barium stearate films have been shown to be promising for making some solid state devices.[1–4] Particularly, in device applications the range of operating voltage is important and therefore a study of the maximum dielectric strength of the films is desirable. Since the devices may be required to operate at various temperatures, it is necessary to investigate the temperature dependence of the maximum dielectric strength. This paper presents a detailed and systematic study of the temperature dependence of destructive d.c. breakdown field in 'built-up' films of barium stearate, not yet reported. Some of the advantages with the films studied are their thermal stability,[5] high dielectric strength,[5] easier reproducibility, uniformity and control of their thicknesses (to 25 Å). The latter have already been very accurately measured.[6] Recently, we have reported a detailed study of the onset breakdown field as a function of temperature.[7] Study of the thickness dependence of the onset breakdown field and static dielectric constant of the films has already been made earlier.[8,9] Chopra,[10] Budenstein,[11–14] Klein[15–17] and their coworkers have also carried out similar and extensive measurements on evaporated film systems to determine the basic mechanism of breakdown conduction in thin dielectric films. This paper presents the refrigerant was employed. The temperatures were measured with the help of a calibrated copperconstanton thermocouple system. The $J-V$ characteristics in the nondestructive phase and the destructive breakdown in the film were studied using mercury drops to contact the aluminium electrodes at both the ends of the capacitor. Direct contact of the aluminium film electrodes by the leads was avoided because of the possibility of disrupting the film from the place of contact. The use of the mercury drop ensures electrical contact even if the film is slightly disrupted.

The measurements of the breakdown voltage are carried out by using a 90 V battery across the sample (sandwich). The voltage is increased from its low values by regulating a linear wire wound potentiometer ($\approx$ 100 K). The breakdown voltage corresponding to the onset of breakdown and the maximum breakdown voltage, were measured with a precision V.T.V.M., having a sensitivity of 0.02 V per division. The maximum uncertainty in the measurements of the breakdown voltage was 0.4 V.

3. RESULTS AND DISCUSSION

Measurements of d.c. maximum breakdown voltage on 20 layer barium stearate films, each of thickness 515 Å, have been carried out in the temperature range -40–40°C. The value used for the thickness of a monolayer of barium stearate is 25.75 Å.[6] Figure 1 shows graphically the temperature dependence of the maximum breakdown field (F_b max) of the Al–Ba.St–Al structure. The breakdown field (d.c.) is found to decrease with increasing temperature. The curve has been obtained using the 'least-squares-fit' of the experimental points. The dots in the graph correspond to the mean values of four or more observations at the same temperature and for the same film thickness of different samples, having almost the same capacitor area (0.4 cm^2). The scatter observed in the experimental data has also been shown in the plot. The destructive breakdown field is of the order of $\approx 10^6$–10^7 V/cm, as reported by Holt.[5]

Figures 2 and 3 are a typical graphical representation of the current density (J) as a function of the applied voltage (V) in the nondestructive phase obtained on barium stearate sandwiches having thicknesses of 515 Å (20 layers), with and without a series resistor (4.7 K). The point A in both the curves correspond to the initial abrupt rise in current, yielding the onset breakdown voltage as has been studied in detail by us[7] recently. The onset breakdown voltage and the maximum destructive breakdown voltage are found to be widely different from each other, for the films studied. Since the theories of electronic breakdown do not include the conduction mechanism after the onset of breakdown, we made no attempt to interpret the above current–voltage characteristics.

Figure 4 shows the dependence of maximum destructive breakdown voltage on the area of the capacitor. The curve has been plotted for a 40 layer (1030 Å thick) barium stearate film, sandwiched between aluminium electrodes, at a fixed temperature 290°K. The breakdown voltage is found to decrease with increase in capacitor area as has also been shown by Budenstein *et al.*[12] in their studies. At present, this dependence of the breakdown voltage on area is not explainable.

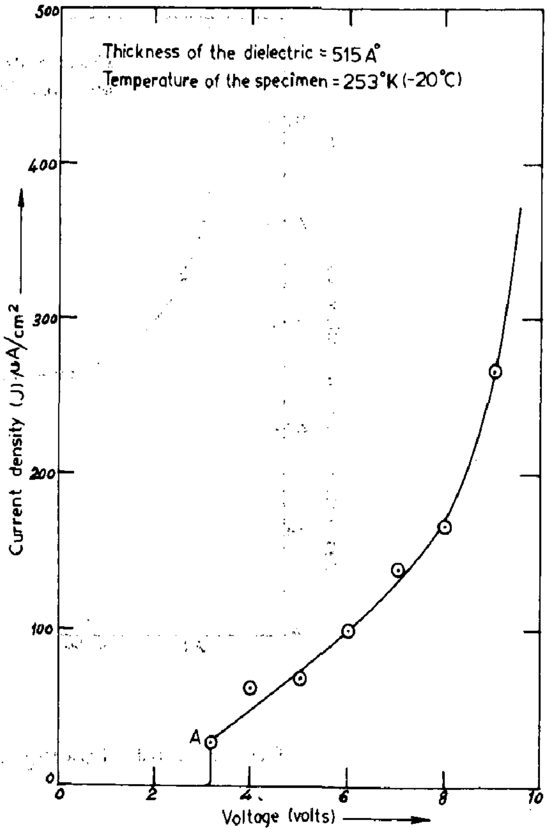

FIG. 2. Current–voltage characteristics at -20°C.

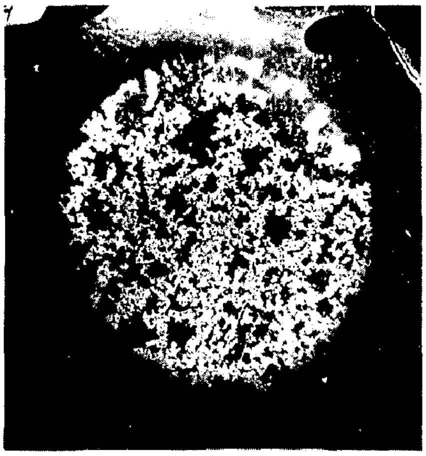

FIG. 5. Transmission photomicrograph showing destruction of the film (X 40).

Figure 5 is a representative transmission photomicrograph (× 40) showing the destruction of the film capacitor of thickness 515 Å (20 layers) over large areas. This destruction may be the result of many 'single' breakdown events. If required, large scale destruction of the film can, however, be avoided by simply cutting off the supply voltage within a few microseconds of breakdown.

The maximum breakdown voltage studied in the present work is not characteristic of the bulk material and is to be distinguished from 'maximum voltage breakdown' observed by Klein and Gafni.[17] As the modern theories of electronic breakdown do not describe the actual mechanism of destruction, no attempt has been made here to interpret the above results theoretically. However, the results may prove useful in the device applications of 'built-up' barium stearate films, involving self-healing, nonshorting capacitor systems.

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On the Validity of Faucher's Ellipsometric Formulae

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Faucher *et al.* [*J. opt. Soc. Am.*, 48 (1958), 51] have given a simplified treatment of thin film ellipsometry and claimed applicability of their theory to much larger thicknesses as compared to those assumed in Drude's approximation. A check of the validity of this claim has been made through corrected calculations on thin films of barium stearate on glass slides coated with vacuum evaporated chromium. It has been observed that the value of 48·8 Å assumed by Faucher *et al.* for the double layer thickness of barium stearate is wrong and the correct value is 51·5±0·6 Å. Recalculation of the values of the parameters using this correct value shows that the agreement between the theoretical and experimental curves is not so good as has been claimed by them.

1. Introduction

DRUDE'S theory[1,2] of ellipsometry of very thin isotropic films is well known for a long time. Faucher *et al.*[3] have recently given a simplified theory of ellipsometry of isotropic thin films based on multiple reflections within the thin film, using only the elementary laws of reflection, refraction and interference. These workers have shown that their results are applicable for much larger thicknesses as compared to those assumed in Drude's approximation. They have found general agreement between their theoretical results and experimental data on 'built-up' barium stearate films consisting of 2-32 double layers (up to thicknesses of 1600 Å). This agreement, however, is based on the use of a value of 48·8 Å for the thickness of a double layer of barium stearate film. But the correct value of the metrical thickness of a double layer, as measured[4] by one of the present authors (V.K.S.) by multiple beam interferometry, is 51·5±0·6 Å. This value of double layer thickness is in excellent conformity with the accurate X-ray measurement on the films[5]. Even the difference of 2·7±0·6 Å in the double layer thickness is significant particularly for films having larger number of double layers, because the ellipsometric parameters have a highly sensitive thickness dependence. In the present paper we have analysed the validity of Faucher's theory by using this correct value of the thickness of the double layer of barium stearate.

2. Faucher's Theory

In Faucher's simplified treatment of ellipsometry, based on multiple reflections within the thin film, the changes produced in the light reflected from the films are calculated by using the model illustrated in Fig. 1.

If a beam of monochromatic light of unit intensity, polarized at 135° to the plane of incidence, is incident at an angle i on a film, Faucher *et al.* show that the point of maximum amplitude is given by

$$\tan x_{\max} = \frac{b(1+a^2)\cos\Delta - a(1+b^2)}{b(1-a^2)\sin\Delta} \qquad \ldots(1)$$

where a and b are the amplitude reflection coefficients at the air-film and film-metal interfaces respectively (Fig. 1) and Δ is the phase difference between any two consecutive reflected beams from the film, corresponding to a given component. Using the above formula, the authors further prove that the resultant reflected intensity is given by

$$I = \frac{a^2+b^2-2ab\cos\Delta}{1+a^2b^2-2ab\cos\Delta} \qquad \ldots(2)$$

The constant a is given by the Fresnel equations as $a_\perp = \sin(i-r)/\sin(i+r)$; $a_\parallel = \tan(i-r)/\tan(i+r)$ where r is the angle of refraction in the film and $a_\perp$ and $a_\parallel$ are the reflection coefficients corresponding to the vibrations perpendicular and parallel to the plane of incidence respectively. The phase difference between the resultants of the two components (parallel and perpendicular to the plane of incidence) is given by

$$\delta = x_{\parallel\max} - x_{\perp\max}$$

Faucher *et al.* have used the method of Drude to take into account the effects due to the metal substrate. Drude's equations which hold for both components are:

$$\left.\begin{aligned} \tan\delta_m &= \sin Q.\tan 2P \\ \cos 2\psi &= \cos Q.\sin 2P \\ b &= \tan\psi \end{aligned}\right\} \qquad \ldots(3)$$

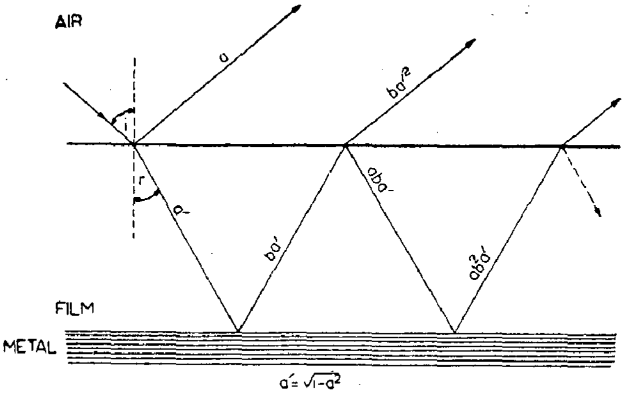

Fig. 1 — The 'multiple reflections' model used to calculate the resultant reflected intensity

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TEMPERATURE DEPENDENCE OF THE BREAKDOWN FIELD IN BARIUM STEARATE MULTILAYER FILMS

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Since “built-up” barium-stearate films seem to be promising for making dielectric devices, it has become essential to study their breakdown characteristics also. The present paper reports a systematic study of the temperature dependence of d.c. breakdown in “built-up” multilayer films of barium stearate in the temperature range −40° to 40 °C. These films are well suited for such studies because of their high dielectric strength, good reproducibility and highly uniform thicknesses which are controllable (to 25 Å) and accurately known. The breakdown field is found to decrease slightly with increasing temperatures. This result cannot be interpreted in terms of the theories of Fröhlich and Callen. Detailed current–voltage characteristics of the films have also been studied in the present work. The data reported on the films may prove useful in their device applications.

INTRODUCTION

“Built-up” films of barium stearate have recently been shown to be promising for making dielectric devices[1–4]. From the point of view of device applications, studies of thickness and temperature dependence of dielectric breakdown in barium stearate films are of crucial importance. Recently one of us reported[5] a detailed and systematic study of the thickness dependence of the d.c. breakdown field in barium stearate films. For these studies the barium stearate films were found to be almost ideally suited because of their highly uniform thicknesses which are controllable (to 25 Å) and accurately known[6]. In addition, these films also possess high dielectric strength and show good reproducibility and thermal stability[7]. In the present work, the temperature dependence of the d.c. breakdown field in “built-up” films of barium stearate, not investigated previously, has been reported. Because of the above mentioned advantages with these films, the latter are well suited for the present studies also. Similar and extensive studies have been carried out in the pioneering work of Budenstein[8–10], Klein[11, 12] and their coworkers on evaporated film systems. Present work also reports the current–voltage characteristics of the film in the non-destructive phase with and without a series resistor.

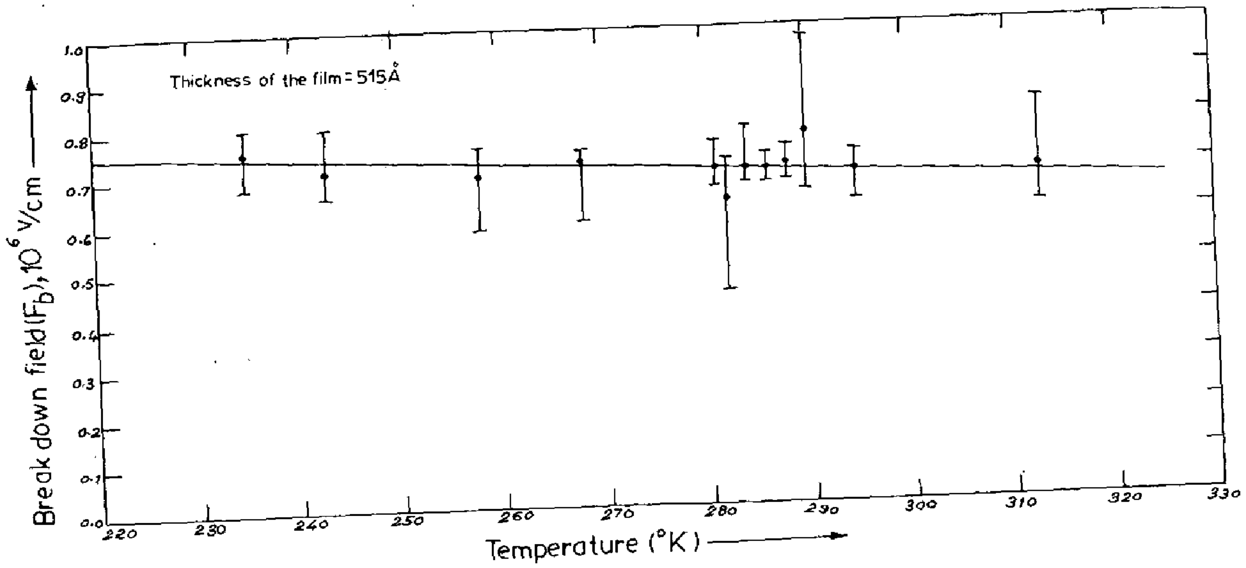

Fig. 2. Plot showing temperature *vs.* breakdown field.

Figure 2 shows graphically the temperature dependence of the dielectric breakdown field of the film. The curve has been obtained using the "least squares fit" of the experimental points. The dots in the graph correspond to the mean values of the four or more observations at the same temperature and for the same film thickness of different samples. The scatter observed in the experimental data has also been shown in the plot. The breakdown strength of barium stearate films for various temperatures is of the order of 10^6 V/cm as reported by Holt[7].

A typical current–voltage characteristic of the barium stearate sandwich at 0 °C is shown in Fig. 3. The point "A" in the plot corresponds to the initial abrupt rise of the current.

Figure 4 shows a representative plot of the current–voltage characteristic of the film at temperature −38 °C with a series resistor (4.7 K).

As can be seen from Fig. 2, the breakdown field decreases slowly with increase in temperature in the range studied. Similar behaviour has been observed by Budenstein and coworkers in some evaporated thin film systems[8–10]. Since the electronic breakdown theories, based on electron–phonon interactions, predict[15] increase of electric strength with increase in temperature, the results of Budenstein *et al.* are unexplainable since they claim the breakdown observed by them to be electronic in nature. The studies of thickness dependence of the breakdown field have already shown[5] the breakdown in barium stearate to be electronic in nature because of close conformity of the results with Forlani–Minnaja's theory[16]. Therefore, in the present studies also, the results cannot be explained in terms of the existing theories. It is thus concluded that the temperature dependence of the breakdown field is, in general, as little understood as the thickness dependence. Since the conduction mechanism in the post breakdown region is also not known, the *I–V* characteristics also could not be explained. However, the results reported in this communication may prove useful in the device application of the films.

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