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Polymer Dielectric Films*

Abstract: Polymer dielectric films, ranging in thickness from less than 100 A to several microns, have become increasingly useful for basic investigations of surface phenomena and thin film electrical conductivity and for thin film electronic device and circuit development. The preparation and characterizing properties of thin polymer films are discussed with particular emphasis on recent developments in such areas as ultraviolet surface photolysis, electron bombardment, gaseous electrical discharge, and special chemical processes. Previously unpublished data on certain aspects of polymer dielectric films are presented, and present and potential applications are briefly reviewed.

Introduction

The dielectric properties of polymeric substances have long attracted the attention of many workers in science, technology and engineering. This interest arises from both a practical and a fundamental point of view. The low electrical conductivity and low dielectric losses which many polymers exhibit make them very useful for electrical insulation and encapsulation. Specific applications, to name only a few, are for capacitors, interconnection insulation, component potting, and encapsulation. From a more basic standpoint, the dielectric properties of polymers offer a tool for studying their molecular structure. Hence there is a great deal of available information on the dielectric behavior of many polymers.[1,2] However, the majority of this data pertains to polymers in bulk form, at least in terms of the definitions to be made below.

The systematization of polymer chemistry is a comparatively recent development, dating approximately from the early part of the second decade of this century; in other words, within the memory of many living chemists. Empirically, of course, polymeric materials in one form or another were employed well before the emergence of polymer chemistry as a branch of science. Hence it is not surprising that the systematic employment of very thin polymer films for their dielectric properties reflects the history of bulk polymers; only very recently has there been any systematic attempt to study these films, though their empirical use extends back over a number of years. These statements are applicable, of course, only if one defines arbitrarily a thin polymer film. The definition employed in this review will now be stated: A thin polymer dielectric film is a solid layer of more or less homogeneous composition which is less than 3μ ($1\mu = 10^4$ Å) thick, uniform in thickness, coherent in structure and adherent upon a supporting surface. The definition foreshadows the primary employment of such films, as capacitor dielectrics, for thin-film circuit insulation, and for basic investigation of electrical conductivity and surface phenomena.

Such thin films are not usually attainable by ordinary coating procedures, and hence suitable means have been devised to produce them. Several surveys discussing the field of dielectric films have been recently published, generally treating polymer films as a subdivision of thin film insulation or of microelectronics in general.[3–6] It is the purpose of this survey to discuss specifically the means of fabricating thin polymer surface films and to describe some of their properties, particularly those concerning dielectric behavior. For this reason much of the material to be covered lies in the province of physical chemistry, and is more process-oriented than theoretical in nature. Because of the variety of techniques employed to produce polymer dielectric films and the rather different purposes for which they have been employed, the nature of the discussion will be expository and not, in general, critical. In addition to material found in the literature, hitherto-unpublished data will be presented and discussed. A brief discussion of present and potential electronic applications of polymer dielectric films will be presented.

General properties

• *Thin films*

Thin dielectric films possess some characteristic properties independent of their composition. Perhaps the most significant property is the fact that the thickness is very small compared to other dimensions; hence the electric field in the insulator can be quite large. Thus the insulator is often

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subjected to field strengths well beyond those at which the bulk material undergoes dielectric breakdown. This phenomenon of increasing dielectric strength with decreasing insulator thickness is well-known and has been discussed extensively by Whitehead,[7] and O'Dwyer.[8] It is generally accepted that when the dimensions of the insulator become smaller than the energetic electron path in the insulator, the dielectric strength increases since avalanche and thermal breakdown are less likely to occur. Thus intrinsic breakdown becomes the predominant mechanism in very thin films.[8] Another aspect of thin-film dielectric behavior is that the actual potential distribution in the insulator at the metal-insulator interface varies over a region which is not negligible compared to the total insulator thickness. Hence the geometric capacitance and the measured capacitance for such a structure may be considerably different. This problem is discussed by Ku and Ullman.[9]

Since the film thickness is small, compared to area coverage, the problem of "pinholes," or regions where the film does not cover the underlying surface, is quite significant. This, of course, is common to all thin films, inorganic as well as organic, but there are several specific points which are worth discussing in detail. Inorganic insulating films are usually produced by deposition techniques such as evaporation, vapor growth, sputtering, etc. The exceptions are materials such as thermally grown SiO_2 and anodic Ta_2O_5. Almost all polymer films are produced by chemical reaction at the surface, either from conversion of monomer to polymer or through an increase in average polymer molecular weight or an increase in polymer crosslinking. Indeed, all three processes may take place in the same film deposition. The important point is that polymer film deposition processes are not self-healing (as, for example, are anodization and thermal oxidation), so great care must be used in substrate preparation and cleanliness to insure that the polymer film can be deposited uniformly over the entire surface. Although there are other contributing factors, the presence of pinholes determines the minimum thickness at which a polymer film will provide reliable electrical insulation. This minimum thickness varies from one type of film and process to another, but is of the order of 100 A. Specific cases will be mentioned later in the discussion of individual films. Second, there are special instances where very thin polymer insulation can be achieved. In the case of a clean metal surface (e.g., Ni) on which a monomer is chemisorbed (e.g., butadiene), the initial polymer formation is roughly analogous to a self-healing process, and extremely thin films which insulate relatively large areas have been obtained.[10] Finally, the absence of large stresses in most polymer films reduces the likelihood of cracking or rupture after deposition. This is a serious problem with many inorganic films.

An important property displayed by thin-film insulators is their ability to conduct appreciable non-ohmic currents due to the mechanisms of electron tunnelling, field emission, space-charge-limited conduction and impurity conduction. The current density J due to tunnelling is given by

$$J = \frac{2.2q^3}{8\pi h}\left(\frac{V}{x}\right)^2\left(\frac{1}{\phi}\right) \times \exp\left[-\frac{8\pi x}{2.96hqV}(2m)^{1/2}\phi^{3/2}\right], \qquad (1)$$

where

q = electronic charge,
V = applied voltage,
x = film thickness,
ϕ = metal-insulator work function,
m = electron longitudinal mass,
h = Planck's constant,

and where the applied voltage V exceeds the barrier height.[11] The current decreases exponentially with increasing thickness, and is usually negligibly small for thicknesses greater than about 100 Å. The emission of electrons by means of the Richardson-Schottky mechanism is more significant, since considerable current can be induced by a large electric field. The current-voltage relationship is expressed by[12]

$$J = AT^2 \exp\,[(q^3V/\epsilon x)^{1/2} - \phi]/RT\,, \qquad (2)$$

where

J = current density,
A = Richardson constant,
q = electronic charge,
V = voltage across the dielectric film,
ϵ = dielectric constant of the film,
x = film thickness,
ϕ = potential energy barrier,
R = gas content, and
T = temperature, °K.

The current density is quite sensitive to temperature. It will be seen later in the discussion of specific polymer films that several examples of this type of current flow in thin polymer films have been claimed. Space-charge-limited (SCL) current is possible for even thicker films, according to the equation:

$$I = K(V^2/x^3)\,, \qquad (3)$$

where

I = current,
V = voltage,
x = film thickness, and
K = constant.

This type of current flow is very sensitive to the presence of trap sites in the insulator. A thorough discussion of SCL currents has been given by Rose and Lampert[13] and Tredgold.[14] Electrical conductivity is also possible in films which contain impurity centers which are capable of ionization; the ions themselves may move under the influence of an electric field, or electrons can "hop" from site to site in the film. Such behavior is often noted in amorphous inorganic dielectric thin films such as silicon nitride.[15] Often this mode of conduction is referred to as the Frenkel-Poole mechanism,[16] and the current density J is given by:

$$J = \phi_0 E \exp\left[\frac{1}{r}\left(\frac{qE}{\pi\epsilon}\right)^{1/2} - \frac{\phi}{r}\right]\frac{q}{kT}, \tag{4}$$

where

ϕ_0 = constant,
E = electric field,
ϵ = dielectric constant,
ϕ = barrier height,
q = electronic charge, and
r = a variable ranging from 1 to 2.

In all of these equations, film thickness is a primary factor in determining the level of electrical conductivity. For very thin films, the current density becomes large enough that destructive heating of the electrodes can occur. In principle, no energy is dissipated in the dielectric for tunnel and emission current, but considerable heating can occur in the latter two types of conduction.

• *Polymer films*

Polymer insulating films are generally prepared by the interaction of a monomeric or low molecular weight polymeric species, usually in gaseous form, with a solid surface in the presence of some form of energy. The energy is often supplied by the thermal energy of the substrate or by radiation; in some cases, it arises from a catalytic reaction involving the surface or resides in the monomer itself. In almost all practical applications, it is desirable or even mandatory that some method for defining the geometric area of the film be available. The resolution required will depend to a large extent on the specific application.

The polymer film should have a low electrical conductivity and a small dissipation factor, with few peaks in the dispersion curve versus frequency. It is desirable that the intrinsic breakdown voltage be high. The dielectric constant requirements depend on the use to which the film is put, but in general this constant is to be kept as low as possible. In all these properties, the polymer films to be discussed vary from good to excellent.

In addition to such general electrical properties, polymer films also have some advantageous physico-chemical features. Thus, many polymer films are able to undergo plastic deformation when a stress is applied, minimizing residual stress in the films. This property also is advantageous in reducing the amount of inherent stress after deposition or growth. One of the important factors in this case is the amorphous structure of most polymers.

Another desirable aspect of polymer films is the use of relatively high-energy deposition processes. Since the energy can be supplied externally, a great degree of generality is obtained in the type of surfaces that can be insulated. Finally, a wide range of these properties is accessible because of the large number of polymerizable species available. In this respect, polymer films may offer unusual properties over and above those pertaining to electrical insulation. These properties would arise from the molecular nature of the polymer. For instance, slight modification of the structure of the monomer could give rise to polymer films with various optical absorption properties, and hence various colored films could be obtained.

There are a number of disadvantages in the use of polymer insulating films as well. Perhaps the most severe is the temperature limitation due to the presence of such relatively labile bonds as C–C and C–H in almost all polymer structures. While advances in the chemistry of polymers may push the maximum temperature limit upward to some extent, polymer films at present are limited to operating temperatures below about 150°C, depending on the specific application, at least for continuous operation. Another problem is the close control and reproducibility of film properties; this will vary from being good for certain formation methods to essentially uncontrollable for others. In some cases, the need for highly specialized equipment is a major problem; in others, it is just the simplicity of the polymer film deposition process which makes these films very attractive.

The chemical stability of polymer films is determined by the nature of the polymer and of the attacking substance. Most are subject to air oxidation at moderate temperatures, while some are readily dissolved by mild solvents at room temperature. On the other hand, certain polymer films are extremely resistant to chemical reaction, while others (usually possessing a conjugated structure) are much more resistant to electron and x-ray irradiation.[17] Most materials are more or less affected by H_2O if the exposure time is sufficiently long and the temperature high enough. The reasons for such a wide variety of behavior are bound up with chemical structure, and in the next section there is a brief discussion of polymerization reaction mechanisms and polymer structure.

Methods of film formation

• *Mechanisms of polymer film formation*

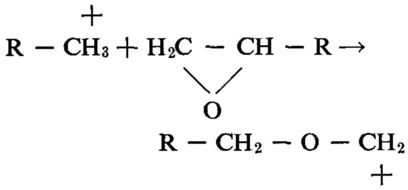
The various specific reactions by which polymer films are formed can be reduced to four processes based not so much on classical polymerization mechanisms as on chemical processes induced by the means of deposition. These are:

1. Addition polymerization: the formation of long chain molecules by the addition of a monomer unit to an already existing polymer molecule. A typical example is the formation of polyethylene:

$$CH_2 = CH_2 + CH_2 = CH_2 \rightarrow CH_2 - CH_2 - CH_2 - CH_2 - (-CH_2 - CH_2 - CH_2)\,CH_2 + CH_2 = CH_2 \rightarrow (-CH_2 - CH_2 - CH_2)_{n+1}CH_2 . \qquad (5)$$

This process usually results in thermoplastic polymers and is associated usually with photolytic processes.

2. Ionic polymerization: the reaction of an ionic species with another ionic or neutral species or molecular site. An example is the reaction of a carbonium ion with an oxirane ring:



$$\overset{+}{R} - CH_3 + H_2C - CH - R \rightarrow R - CH_2 - O - CH_2 - \underset{+}{R}H_2 - R . \qquad (6)$$

This reaction has been postulated to be the mechanism of epoxy film formation during electron bombardment.

3. Recombination polymerization: the production of a solid polymer film of amorphous structure by the creation of numerous reactive species in an energetic process such as a gas discharge:

$$R_1 - R_2 + R_3 - R_4 \rightarrow R_1^* + R_2^* + R_3^* + R_4^* \rightarrow [-R_4 - R_2 - R_1 - R_3 -] . \qquad (7)$$

This is the least specific mechanism, and the resulting films are correspondingly the least well characterized and most highly cross-linked.

4. Condensation: This is not the same as condensation polymerization in the bulk, which involves the splitting out of H_2O, etc. Rather, it refers to the condensation on a surface of a polymer species to form a film which is basically a low molecular weight, low vapor pressure material. An example is the vacuum evaporation of a polymer by thermal means followed by condensation on a surface.

All of the polymer films to be discussed are formed by one or more of these basic mechanisms.

• *General processes for polymer film formation*

The formation of polymer insulating films can be accomplished by a number of processes. These include:

1. Gaseous discharge
2. Electron bombardment
3. Photolysis
4. Pyrolysis
5. Non-energetic deposition

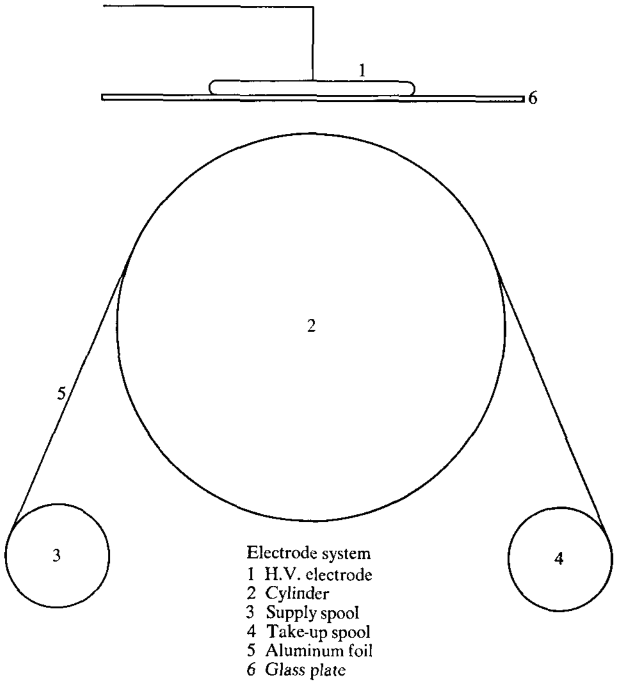
This classification mostly excludes such processes as spraying, casting, sintering, dipping, electrophoresis, etc. since these are generally useful only for much thicker polymer layers and do not produce films free of voids or pinholes at micron thicknesses. All the processes listed above have several common characteristics; for instance, they require some sort of controlled atmosphere, ranging from a high vacuum to a moderately low partial pressure of monomer. Also, the substrate surface almost always plays a passive role, in the chemical sense, for these techniques. This feature distinguishes polymer dielectric films from another major category of thin film insulation, which is the thermally (or anodically) produced metal oxide or semiconductor oxide surface film widely used in semiconductor electronics and in basic research involving electron transport across interfaces.[18,19]

The properties of a polymer film are largely dependent on the nature of the deposition technique. For example, polydivinylbenzene films can be produced from divinylbenzene (DVB) vapor by any of the first four processes, but the properties of the resulting films will be somewhat different in each case. The similarity of a polymer film's properties to those of its bulk polymer analogue is least for process No. 1, and becomes closer for each succeeding process No. 2 through No. 5.

• *Gaseous discharge*

The observation that silent or "glow" discharges in various organic vapors resulted in the formation of insulating films on surfaces exposed to the discharge was made many years ago. This phenomenon posed an annoying problem in the operation of relays and switches and is discussed in some

Figure 1 Schematic diagram of continuous deposition dc glow discharge polymerization system.[25]



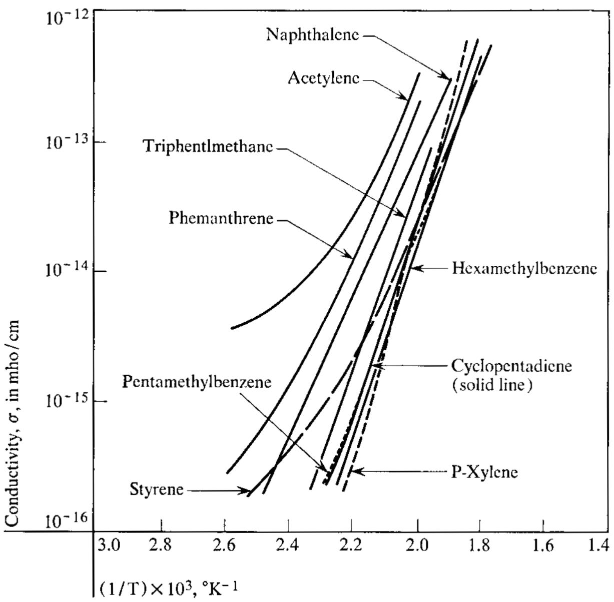


Figure 2 Log electrical conductivity of polymer films derived from hydrocarbons vs. reciprocal temperature.[22]

of the work on electrical contacts.[20] The acceleration of electrons and ions in an electric field causes collisional excitation of the organic molecules to elevated electronic levels as well as direct ionization, and wall recombination of these ions, radicals, and excited molecules is responsible for the buildup of the polymer film. This technique was first deliberately applied to produce useful insulating films by Goodman.[21] He used a pair of parallel electrodes immersed in an organic vapor, and by applying a sufficiently large potential difference to the electrodes he obtained a glow discharge that resulted in polymer film deposition on the electrodes. By placing the desired substrate on one of the electrodes, he was able to coat it with polymer film to the desired thickness. A typical apparatus meant for continuous deposition is shown schematically in Fig. 1. This method of film formation gave high deposition rates for a large number of organic molecules, not all of which are monomers in the usual chemical sense. The parallel-plate method was extended by Bradley and Hammes to a highly varied number of materials, and the conductive and photoconductive properties of the polymer films were extensively measured.[22,23] The conductivity-temperature behavior of some of these polymers is shown in Fig. 2.

Further investigation of the photoconductivity of glow-discharge polymer insulating films by Bradley led to the proposal[23] of indirect activation of carrier sites in the film to explain the observed behavior.

The dc technique has several disadvantages. Relatively high gas pressures are required, and there is considerable substrate heating. Thus, the films are not well defined geometrically. In addition, the reproducibility of film structure and composition is not good, due to the variety of recombining species and the possibility of contamination of sputtering of parts of the system. (On the other hand, the films are hard, durable and are quite suitable for the production of rolled-film capacitors.) Attempting to minimize these problems, DaSilva and Miller used an oxide-coated cathode to inject electrons into the gas phase and sustain a glow discharge near the anode, which contained the surface to be covered.[24] The gas used was 1,3 butadiene. Under these conditions, stencil masking was somewhat more effective for geometric definition, and radiation from the hot cathode was the main source of substrate heating. The polymer films obtained were hard and strong and hence were probably crosslinked polybutadiene.

The properties of insulating films prepared by an ac glow discharge in styrene vapor have been studied extensively by Stuart.[25,26] The effects of the presence of other gases (O_2, N_2, H_2) during the discharge on the dissipation factor of the polymer films was examined in some detail. The dissipation factor of the films was higher than would be expected for polystyrene, and was attributed to residual trapped free radicals in the film.

A detailed account of polymer film formation on the electrode surfaces in contact with an ac glow discharge sustained in various monomer vapors has been published by Williams and Hayes.[26] Considerable attention is paid to analyzing the glow discharge system electrically, and relating the parameters to the mechanism of film formation. The authors speculate that the polymer film results from activation of the adsorbed monomer by ionic bombardment of the surface. The conclusion is that cross-linked, high molecular weight polymers are formed and that activation and/or polymerization in the gas phase is not a significant part of the process. Very high deposition rates, up to 8 μ/min, were reported.

Another type of ac discharge process was employed by Cornell and Gregor to reduce substrate heating and shadowing effects even further.[27] The system, shown in Fig. 3, employed rf electrodeless excitation of a discharge inside a tube through which monomer gas was flowing. By applying a longitudinal magnetic field with a Garret coil concentric around the tube, the efficiency of the discharge was increased; i.e., less power input was needed to sustain the glow. The traveling glow then impinged on the surface where the film was desired. Thus the surface played a completely passive role. A summary of the conductive properties of various gaseous discharge films is given in Table 1, taken from Bradley and Hammes.[22] It is interesting to note the chemical diversity of the monomers.

Recently, a detailed investigation has been made of the infrared spectra of polymer films obtained by glow discharge in various hydrocarbon vapors.[28] The results were extensively interpreted by assigning the various bands to particular vibrational modes. The structure of the films was

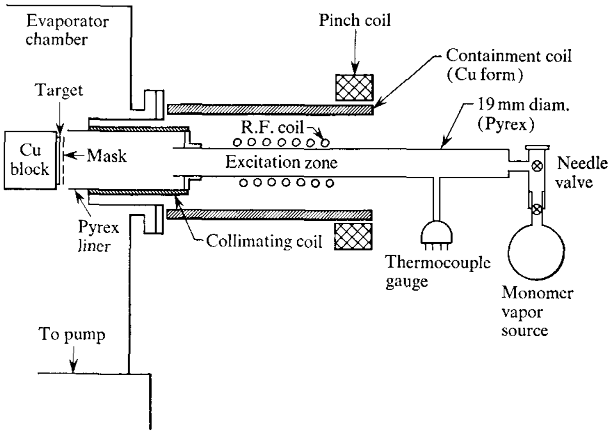


Figure 3 Schematic cross-sectional diagram of magnetically focused glow discharge apparatus.[27]

quite different from that of conventional polymers prepared from the same monomers. Considerable unsaturation was observed in the structure of polymer films obtained from n-pentane and ethylene for example. Also, evidence was found for RC ≡ CR and R ≡ CH triple bonds in the polymer obtained from benzene vapor. This seems to substantiate the extensive decomposition of the parent molecule in the glow discharge, followed by recombination to form a cross-linked, unsaturated polymer on the substrate surface.

An interesting comparison of the properties of polystyrene films produced by a glow discharge (GDP) with commercial bulk polystyrene has been made by Carbajal (Table 2).[29] Films prepared at the higher pressure were more unstable.

The mechanisms by which solid films are produced from a gaseous discharge have not been studied in detail. Because of the ability of substances such as benzene selenol and thiourea to yield polymeric films, the mechanisms are obviously more complicated than simple addition or condensation reactions.[22] The rather similar polymer electrical properties found for a very diverse array of gases indicates considerable breakup of the original molecular structure of the monomer, followed by reformation of the C–C bond as the fragments collide with each other or the wall. It has been observed that increasing the power dissipation in the discharge generally leads to discoloration of the film, indicating that the C–H bond begins to dissociate if sufficient energy is provided.

Recently, the deposition of inorganic insulating films has been accomplished by the sputtering of material from a cathode subjected to ion bombardment from an rf plasma, which is a glow discharge in the general sense.[30] No published accounts are available concerning polymer films obtained by this technique but the sputtering of polymer films certainly seems to be an area worthy of further study.

Table 1 Typical conductivity vs. temperature data.

Monomer	*Conductivity, mho/cm.*		*Activation energy,* eV
	150°	250°	
Naphthalene	9×10^{-16}	2.7×10^{-13}	1.1
Styrene	6×10^{-16}	9×10^{-14}	1.2
p-xylene	5×10^{-17}	1.5×10^{-13}	1.8
Cyclopentadiene	1.0×10^{-16}	1.2×10^{-13}	1.5
Hexomethylbenzene	7×10^{-17}	7×10^{-14}	1.5
Ethylene oxide	4×10^{-16}	1.6×10^{-13}	1.1
Methoxynaphthalene	1.1×10^{-16}	7×10^{-14}	1.5
Thiourea	3.3×10^{-16}	4×10^{-13}	1.7
Chlorobenzene	8×10^{-17}	1.9×10^{-14}	1.4
Picoline	2.2×10^{-14}	6×10^{-12}	1.1
N-nitrosodiphenylamine	8×10^{-15}	3.0×10^{-12}	1.2
p-toluidine	7×10^{-16}	2.3×10^{-12}	1.5
Aniline	2.8×10^{-16}	1.4×10^{-12}	1.8
p-nitrotoluene	5×10^{-16}	2.5×10^{-13}	1.2
Diphenyl selenide	3.1×10^{-18}	8×10^{-13}	0.75, 1.5
Diphenyl mercury	2.8×10^{-15}	2.7×10^{-13}	0.85
Ferrocene	2.7×10^{-13}	4.5×10^{-12}	0.55
Benzene selenol	2.5×10^{-14}	7×10^{-12}	1.1
Hexa-n-butyl (di) tin	1.5×10^{-15}	7×10^{-13}	1.1
Tetracyanoethylene	1.8×10^{-13}	5×10^{-12}	0.60
Malononitrile	3×10^{-14}	1.8×10^{-12}	0.75
Thianthrene	1.5×10^{-14}	1.6×10^{-12}	0.85
Thiophene	6×10^{-14}	3×10^{-12}	0.75
Thioacetamide	8×10^{-14}	9×10^{-12}	0.85

Table 2 Comparison of GDP styrene and polystyrene.

	GDP styrene	*GDP styrene II*	*Polystyrene*
Dielectric constant	2.90	2.93	2.5 to 2.7
Refractive index	1.60	1.70	1.592 to 1.597
Resistivity, ohm-cm	10^{16}	10^{16}	10^{17} to 10^{19}

- *Electron bombardment*

Electron beam-induced polymerization on surfaces was first observed accidentally in earlier electron microscope investigations. The source of the polymer was attributed to the interaction of electrons (presumably low-energy scattered or secondary electrons) with the residual pump oil vapors in the vacuum system. Although this process was observed and understood as a nuisance by Ennos[31] and by Poole,[32] several years elapsed before this phenomenon was proposed as a means for producing useful thin film electrical insulation for circuit fabrication.[33] Since then, more and more detailed investigations have been performed.

The polymerization of DC-704 pump oil, which is basically a low molecular weight polydimethyldiphenylsiloxane, was systematically studied by Christy.[34] By studying the rate of growth of the film as a function of the oil vapor pressure, the electron accelerating voltage and current density, and temperature, he developed a phenomenological theory to describe the process. Briefly, it is assumed that an electron interacts with an absorbed oil molecule to create a reactive site which then allows the molecule to cross-link with another adjacent molecule. There are two limiting cases. (1) The rate of film growth is determined by the rate of arrival of oil molecules, the low pressure limit, in which case the rate of growth is given by the expression

$$R = \frac{vF}{1 + 1/\delta\tau f}, \tag{8}$$

where R is the rate of film formation, F is the number of oil molecules striking the surface per unit area per unit time, v is the volume of one molecule, δ is the cross section for a cross-linking collision, τ is the mean stay time of an oil molecule, and f is the electron flux per unit area per unit time. At high current density or low temperature, $\delta\tau f \gg 1$, and the rate approaches a saturation value vF, determined by the effective vapor pressure. At the other extreme (high temperature or low current density), the rate is approximately

$$R = \delta f v F, \tag{9}$$

and thus still dependent on current density and temperature. The other case is (2) when there is always a monolayer of oil molecules waiting to be struck by electrons (high pressure limit). In this case, the rate is given by

$$R = (\delta/a)vF, \tag{10}$$

where a is the area of an oil molecule. Here the rate is independent of oil pressure.

A detailed investigation of secondary electron emission from the polymer surface during bombardment was conducted by Mann for DC-704 pump oil.[35] He observed a dependence of growth rate on secondary electron emission. The reasons for this are not clear, but presumably the low-energy secondary electrons are quite effective in activating the silicone molecules on the surface or in the gas phase; i.e., the cross-section for effective electron-molecule collision increases with decreasing electron energy. An earlier publication by Mayer concerning the formation of films in an electron microscope showed that electron energies as low as 6 eV could be effective in causing film formation from residual vacuum pump oil molecules.[36]

The work on DC-704 was subsequently extended by the same authors[37,38] to include the properties of the thin polymer insulating layers. Both Christy and Mann observed non-ohmic conductivity at large applied voltages, the former using films in the range 50–150 Å thick, and the latter 500–2500 Å. For the thinner films, Schottky emission and distributed electron traps in the dielectric seemed to be the mechanism, while for the thicker films the conductivity was more complex in behavior.

A detailed investigation of the properties of insulating films produced by electron bombardment of dimethylpolysiloxane vapor has been published by Hill.[39] Measurements were made of the dc resistivity and of capacitance changes on aging. It was concluded that these films had great promise for applications in cryogenic microcircuitry.

It was concluded by Holland and Laurenson that silicone vacuum pump oil was not as useful a material for producing dielectric films by electron bombardment as the polymethylsiloxanes. They have reported electrical data on polymerized DC-704 films as a function of electron energy, bombardment time, substrate temperature, and presence of other gases.[40]

Other materials have been polymerized by electron bombardment, including butadiene,[41] styrene,[42] methyl methacrylate,[43] and other more complex molecules. Fotland and Burkhardt obtained polymer films by electron bombardment of adsorbed styrene.[42] They achieved only a very low rate of deposition, and it is possible that either high substrate surface temperature or low arrival rate or mean stay time of styrene on the surface was responsible. Haller and White bombarded 1,3 butadiene and obtained polymer films, again at a low rate.[41] By using an oscillating crystal as the substrate, they were able to monitor deposition rates accurately. Their analysis of the kinetics of film growth seemed to point to an ionic polymerization mechanism, but free-radical addition polymerization could not be ruled out.

Since free radical vinyl addition is a possible mechanism, the rate of deposition may be independent of electron energy or current density (at least over wide ranges of these variables) if the monomer can polymerize via such a route. This speculation is strengthened by the results of DaSilva and Klokholm with divinylbenzene.[43] By using directional gas inlet jets and regulating the substrate temperature with a heat sink, they were able to achieve polymerization rates as high as 3100 Å/min at −80°C substrate temperature. The rate of deposition was essentially independent of beam current density and the data were fitted by an empirical equation:

$$r = \phi^n k_0 \exp\left[-Q/kT\right], \tag{11}$$

where r is the rate of deposition, ϕ is the effective partial pressure of monomer at the substrate, n an empirical constant approximately 0.5, Q an energy term equal to 15 kcal/mole, and kT has its usual significance. Since Q is positive, it is probably related to the heat of condensation of the monomer on the surface. The experimental difficulty associated with controlling substrate temperature, and the tendency for unpolymerized material to be retained in the polymer film are inherent in this process. To avoid such problems, Brennemann and Gregor prepared polymer films by electron bombardment of an evaporated epoxy resin.[44] The bombardment and evaporation were done simultaneously with an experimental arrangement shown in Fig. 4.

Table 3 Dielectric properties of polymerized epoxy resin films at 23°C and 1 kHz.

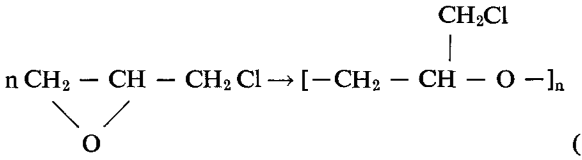
Sample	*Measured thickness,* Å	*Capacitance, pF*	*Dielectric constant*	*Dissipation factor*	*Dielectric strength, V/cm*
2-44-3	2400	581.8	5.7	0.0063	−(n.m.)
3-47-3	2680	563.4	6.2	0.0070	−(n.m.)
4-50-3	1980	652.2	5.3	0.004	$\geq 1.9 \times 10^6$
2-42-3	1630	1368	5.4	0.0062	$\geq 1.2 \times 10^6$

The rate of film deposition was primarily a function of the rate of evaporation of the epoxy resin, since the electron/monomer ratio was high, approximately 350. The resulting polymer film possessed useful dielectric properties (Table 3) and appeared to be an amorphous, highly cross-linked polyphenylmethylsiloxane.

The nucleation of metallic films on poly-epoxy films depends on the nature of the surface. While nucleation and growth occur readily on the polymerized surface, no growth occurs on unpolymerized surfaces. Caswell and Budo were able to form metallic film patterns by exposing the evaporated epoxy resin film to electron bombardment through a mask.[45] Subsequent evaporation of tin and indium resulted in metallic film deposition on exposed areas only. Similar effects were obtained by illumination of the epoxy surface with ultraviolet light.

Thornley and Sun have polymerized photoresist with an electron beam and formed a coherent cross-linked polymer layer which may have some useful dielectric properties.[46] One of the more interesting points of this technique is the high degree of resolution of the film pattern which is obtained, as low as one micron.

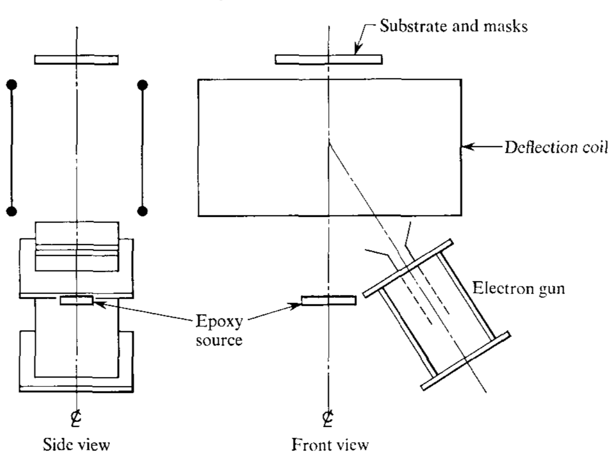
Because the presence of residual OH groups in poly-epoxy films may contribute to low-frequency dielectric losses or may be slowly reacting with time, Gregor and Kaplan chose epichlorohydrin, one of the precursors of Epon 828, as the monomer to polymerize with an electron beam.[47] The reaction schematically may be written



$$n\,CH_2 \underset{\diagdown\ O\ \diagup}{-} CH - CH_2Cl \rightarrow [-CH_2 - \overset{CH_2Cl}{\overset{|}{CH}} - O -]_n \qquad (12)$$

Although the rate of deposition was quite low, insulating films were obtained at thickness of 100 Å and 64 Å.

Figure 4 Apparatus for simultaneous evaporation and electron bombardment of epoxy resin.[44]



The electron bombardment of several pump oil vapors and an epoxy resin vapor has been described by Allam, et al. as a practical process for insulation of cryotron circuits.[48] They report that the polymer films obtained had a minimum reliable thickness (on Pb films) of 100 Å.

It has been observed that the potential distribution at the surface and in the interior of the depositing films is dependent on the accelerating voltage and the grounding of the substrate metallic films. This had led occasionally to internal arcs or discharges between metallic films. The problem has recently been studied in some detail by Geddes.[49] He observed that isolated metallic films equilibrated to a negative potential during exposure to the beam. In device fabrication, the potential of all metal areas must be controlled at ground or a few volts positive to avoid uneven polymer films or damage. The equilibrium potential was also highly dependent on the monomer partial pressure; typical data for p-xylene are shown in Fig. 5.

An interesting variation has been reported by Woodman,[50] who prepared polymeric siloxane films by electron bombardment of evaporated triphenyl silanol. These films were then converted to amorphous SiO_2 by oxidation in air at 500°C.

- *Photolytic reactions*

The formation of polymer films on the walls of a vessel containing methyl methacrylate vapor under illumination from an ultraviolet source was first observed by Melville.[51] After an extensive investigation, he concluded that the monomer was being excited by absorption of light in the gas phase, and after undergoing vinyl addition polymerization the polymer finally deposited from the gas phase onto the wall. This observation was noted by White[52] two decades later, and he proposed using a molecule which would

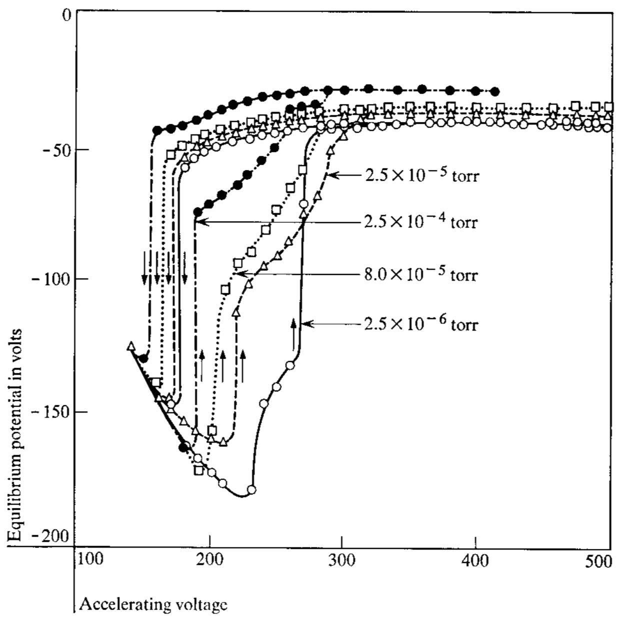
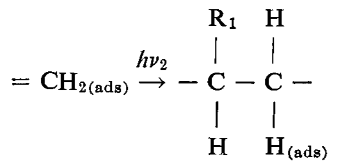


Figure 5 Equilibrium potential vs. electron beam accelerating potential for various pressures of monomer.[49]

be chemisorbed on a surface, thus shifting the frequency of light for activation from ν_1 in the gas phase to ν_2 for the adsorbed phase:

$$R_1CH = CH_{2(gas)} \xrightarrow{h\nu_1} R_1CH$$



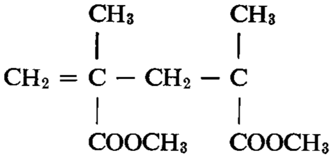
$$= CH_{2(ads)} \xrightarrow{h\nu_2} -\overset{R_1}{\underset{H}{C}} - \overset{H}{\underset{H_{(ads)}}{C}} - \qquad (13)$$

He was able to produce thin insulating films by this technique.

Recently, the preparation and properties of very thin polymer layers obtained by ultraviolet photolysis of adsorbed butadiene has been discussed by White.[53] The polymer thickness varied from 500 to 600 Å, and capacitance measurements were employed to examine the dielectric constant and dissipation factor of the films.

$$CH_2 = C(CH_3)COOCH_3 \xrightarrow{h\nu} CH_2^* = C(CH_3)COOCH_3$$

$$CH_2^* = C(CH_3)COOCH_3 + CH_2 = C(CH_3)COOCH_3 \rightarrow$$



$$CH_2 = \overset{CH_3}{\underset{COOCH_3}{C}} - CH_2 - \overset{CH_3}{\underset{COOCH_3}{C}} \qquad (14)$$

and so on to produce a linear polymer. This means that the

Table 4 Some typical electrical properties of polymer dielectric films.

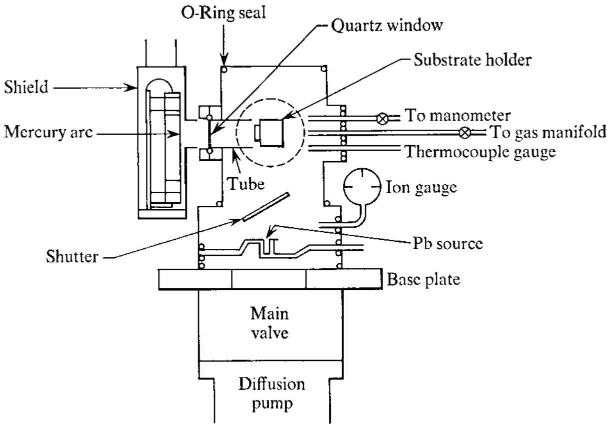
	Monomer		
	Methyl methacrylate	*Acrolein*	*Divinyl benzene*
Dielectric constant at 1 kHz and 25°C	3.5 ± 0.35	3.5 ± 0.3	3.2 ± −.2
Dissipation factor, avg., 500 Å	0.038	0.030	0.005
Dissipation Factor, avg., 4000 Å	0.11	0.09	0.012
Breakdown voltage, V/cm	2×10^6	3×10^6	5×10^6
% samples initially reliable	76[1]	94	98
Stable on thermal cycling, 77°K–298°K	yes	yes	yes
Probable cross-linking	uncertain	yes[2]	yes

1. Reliable insulation produced only when a photoinitiator was used.
2. Polymer film insoluble in liquid monomer.

polymer has a low softening temperature and, being polar, has a relatively high dissipation factor.

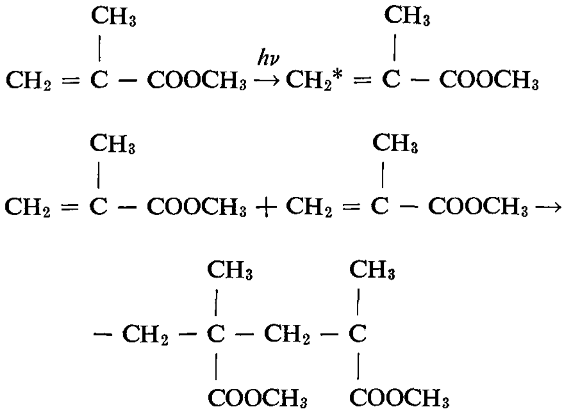
The photolysis of a number of other materials was investigated by Gregor and McGee, who examined the behavior of methyl methacrylate, acrolein, divinylbenzene, etc.[54–56] The experimental system (Fig. 6) employed a 500 watt, medium-pressure mercury arc whose output of 120 watts between 2000 and 4000 Å entered the bell jar through a quartz window. The distance from the arc center to the substrate was 21 cm. The substrate was clamped in a recess cut into a hollow copper block, which entered the bell jar 90° from the axis of the light beam. The temperature of the substrate was regulated to ±2°C. A set of masks

Figure 6 Schematic diagram of ultraviolet photolysis system.[54]



was held in place 0.010 in. above the substrate and manipulated by an actuating rod. The substrate could be rotated through 360° in the vertical plane and thus made to face either the light beam or the metal evaporation source. Some of the dielectric properties of these photopolymerized films are given in Table 4.

Of all the polymer film deposition processes, ultraviolet irradiation is the most specific in terms of producing a polymer whose properties are related to those of both the parent monomer and the bulk polymer. This is because the energy of the photons absorbed by the monomer is sufficient to produce only the excited electronic state from which the molecule reacts to form the polymer. Thus, in the case of methyl methacrylate, the reaction is:



$$CH_2=\overset{\overset{CH_3}{|}}{C}-COOCH_3 \xrightarrow{h\nu} CH_2{}^*=\overset{\overset{CH_3}{|}}{C}-COOCH_3$$

$$CH_2=\overset{\overset{CH_3}{|}}{C}-COOCH_3+CH_2=\overset{\overset{CH_3}{|}}{C}-COOCH_3 \longrightarrow$$

$$-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}$$

It has been reported that dielectric films have been obtained, by photolysis of hexachlorobutadiene, which possess greater thermal stability and chemical inertness than the conventional polybutadiene films.[56a]

In order to increase the thermal stability of a polymer film, one can also utilize a monomer which is directly polyfunctional, such as divinylbenzene, or is capable of reacting at a second part of the molecule as well as at the double bond, such as acrolein. The latter is known to form cross-linked bulk polymer when irradiated by γ-radiation. When it is deposited as a thin film by ultraviolet irradiation, the degradation temperature is about 200°C. Further evidence for cross-linking through the aldehyde group is provided by the infrared spectrum of the polymer film (Fig. 7).

The following mechanism of polymerization of acrolein has been proposed by Gregor and McGee.[55] A detailed mechanism for the formation of a polymer film on a surface when monomer vapor and surface are exposed to ultraviolet light may be written:

(1) $M_{(\mathrm{gas})} = M_{(\mathrm{ads})}$.

(2) $M_{(\mathrm{gas})} + f(I) \xrightarrow[k_2]{h\nu} M^*_{(\mathrm{gas})}$.

(3) $M_{(\mathrm{gas})} + f(I) \xrightarrow[k_1]{h\nu} M^*_{(\mathrm{ads})}$.

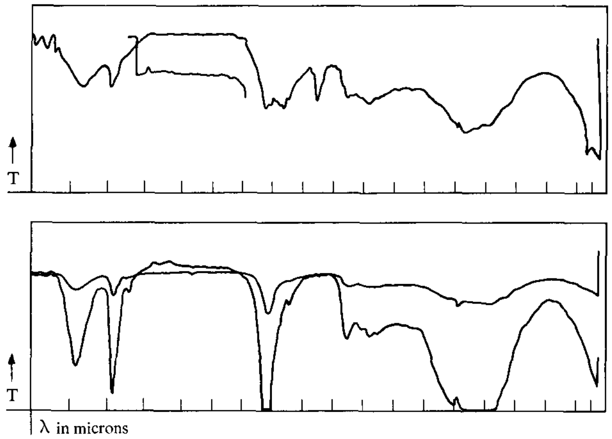


Figure 7 Infrared spectra of polyacrolein films photolysed (top) with nitromethane; (bottom) without nitromethane.[55]

(4) $M^* + M \xrightarrow{k_3} P^*$.

(5) $P_n{}^* + M \xrightarrow{k_n} P_n{}^* + 1$.

(6) $P_m{}^* + P_n{}^* \xrightarrow{k_t} P_{\mathrm{inactive}}$.

(7) $P_m{}^* + M^* \xrightarrow{k_t} P_{\mathrm{inactive}}$.

M and M^* stand for a ground-state and an excited monomer molecule; P^*, $P_n{}^*$ and $P_m{}^*$ are activated polymer molecules of varying chain lengths, P_{inactive} is a terminated or nongrowing polymer molecule and $f(I)$ is proportional to the light intensity. In this mechanism, the activated species is assumed to be a free radical, and chain transfer is neglected.

If (1) is a physical adsorption process, it may be assumed to be fast enough for equilibrium to be achieved at the pressures and temperatures employed here. Since physical adsorption does not significantly alter bond strength, $k_1 = k_2$. Gas-phase activation is assumed to be a constant factor in the region near the substrate. Therefore, only (3) will be considered. In (4) and (5), the complete expressions for the consumption of M by these reactions are sums:

$$-\frac{d(M)}{dt} = \sum_{n=1}^{n} k_n P_n{}^* M . \qquad (15)$$

A reasonable assumption is that $k_3 = k_4 = \cdots = k_n$, and thus all the $P_n{}^*$ and M^* can be written interchangeably. Finally, the reaction scheme for the formation of the film is:

1. $M_{(\mathrm{gas})} \overset{K}{=} M_{(\mathrm{ads})}$ (fast equil).
2. $M_{(\mathrm{ads})} \xrightarrow[k_1]{f(I)} M^*$; $k_1 f(I) M_{(\mathrm{ads})}$.
3. $M_x{}^* + M \xrightarrow{k_2} M_x{}^*{}_{+1} k_2 M_2{}^* M$.
4. $M_x{}^* + M_y{}^* \xrightarrow{k_3} P k_3 (M_x{}^*)^2$.

The steady-state approximation results in a rate law:

$$-d(M)/dt = k_1 f(I)[M_{(\mathrm{ads})}] + k_2[(k_1/k_3)f(I)(M)]^{1/2}. \quad (16)$$

However, the rate of polymerization R_p is actually given by the rate at which molecular units are incorporated into the film, which is the second term on the right; therefore

$$\begin{aligned} R_p &= k_2[M]\left(\frac{k_1}{k_3} f(I)[M]\right)^{1/2} \\ &= k_2\left(\frac{k_1}{k_3}\right)^{1/2} f(I)^{1/2}[M]^{3/2}\,, \qquad (17) \end{aligned}$$

which is the rate law for bulk polymerization.[57] However, since adsorption equilibrium is maintained at all times, we can estimate the number of molecules striking a unit area per unit of time at a pressure of 5 mm Hg from the gas kinetic equation:[58]

$$N = p(2\pi mkT)^{-1/2}\,. \qquad (18)$$

For $p = 5$ mm Hg and $T = 273°$K, $N = 5.68 \times 10^{19}$ molecules/sec cm^2, while under the same conditions, the rate of formation of polymer corresponds to 5×10^{12} molecules of monomer being incorporated per cm^2 per second. Therefore, it may be assumed the M in both gas and adsorbed phases is essentially unchanged because of the high concentration. Then from the previous equations of the reaction scheme, the steady-state approximation leads to

$$\begin{aligned} \frac{d(M)}{dt} &= k_1 f(I) - k_3[M^*]^2 = 0\,, \\ M^* &= \frac{k_1}{k_3} f'(I)^{1/2} \\ R_p &= k_2[M]\,, \qquad \text{and} \\ [M^*] &= k_2 \frac{k_1^{1/2}}{k_3} f'(I)^{1/2}[M]\,, \qquad (19) \end{aligned}$$

or a pseudo first-order dependence of rate on monomer concentration. The data are in agreement with this hypothesis, as is the assumption that the rate is proportional to the square root of the light intensity.[55]

From either Eq. (17) or Eq. (19), the overall activation energy E_a for the reaction is given by

$$E_a = \tfrac{1}{2}\Delta E_1 + \Delta E_2 - \tfrac{1}{2}\Delta E_3 + \Delta H_{(\mathrm{ads})}\,, \qquad (20)$$

where $\Delta H_{(\mathrm{ads})}$ is the heat of physical adsorption. We assume reasonable values for the variables to be

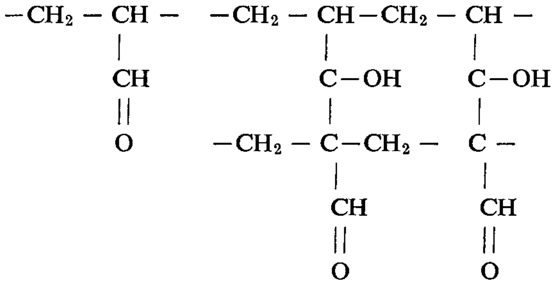
$$\begin{aligned} \Delta E_1 &= 115 \text{ kcal/mole,} \\ \Delta E_3 &= 0, \\ \Delta H_{(\mathrm{ads})} &= +10 \text{ kcal/mole,} \\ \Delta E_2 &= -17 - 57.5 + 10 \text{ kcal/mole, and} \\ E_2 &\geq -63 \text{ kcal/mole.} \qquad (21) \end{aligned}$$

Such a value may explain the relative inefficiency of the process with respect to the average quantum yield. The output of the lamp is approximately 8×10^{12} quanta sec^{-1} cm^2 at the substrate, and the number of molecules polymerized is 5×10^{12} molecules cm^{-2} sec.$^{-1}$ These figures are obtained by considering the output of the lamp at wavelengths shorter than 2600 Å and choosing a rate of 60 Å/min. Thus, the overall quantum yield is of the order of unity, even though it has been observed that typically a higher yield is obtained in bulk photopolymerization of acrolein.[59] This is interpreted to mean that the rate-determining step involves the reaction of an absorbed acrolein molecule with the free radical, be it a growing chain or a monomer radical. The activation energy is sufficiently high that it is apparent that some method of preheating the monomer while still retaining the longer absorption residence time afforded by a cooled surface would better optimize the process. This is observed when the gas is heated slightly by a source of heat in the system.[56]

At acrolein partial pressures above 5 mm Hg, the rate of film deposition appears to have reached a limiting value which is probably determined by the number of quanta reaching the surface. Experiments performed at higher pressures (up to 20 mm Hg) showed no significant difference in the limiting rate, indicating that gas-phase absorption of radiation is not an important factor, at least in this pressure range.

The cross-linking of the polymer can be inferred from the direct evidence that the polymer does not soften and flow upon heating and from the insolubility of the polymer in solvents such as acetone and even in its monomer. This is in agreement with the interpretation given by Schulz and his coworkers.[60] The infrared spectra of the films polymerized in the presence and absence of nitromethane show very little difference, indicating that nitromethane is not instrumental in achieving cross-linking.

The presence of an infrared absorption band at 2.95μ might be attributed to an $-$OH stretching mode if a hydroxyl group is formed during the polymerization. This could happen, for instance, by transfer of a tertiary hydrogen atom on one chain to the aldehyde group of an adjacent chain:



The migration of an $-$H atom from a $-CH_2$ group to achieve the same sort of cross-linking seems less likely. This structure accounts for the presence of an infrared band at 2.95μ. However, it is clear that other cross-linked structures are possible; in fact, other structures must be invoked

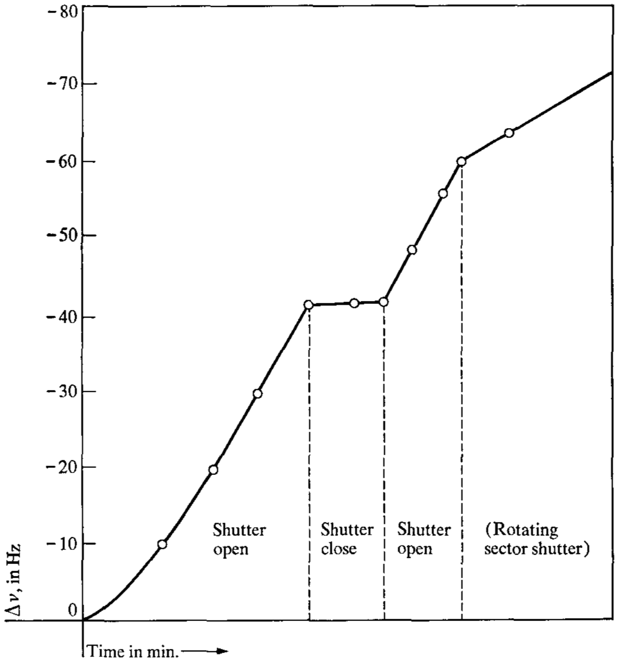
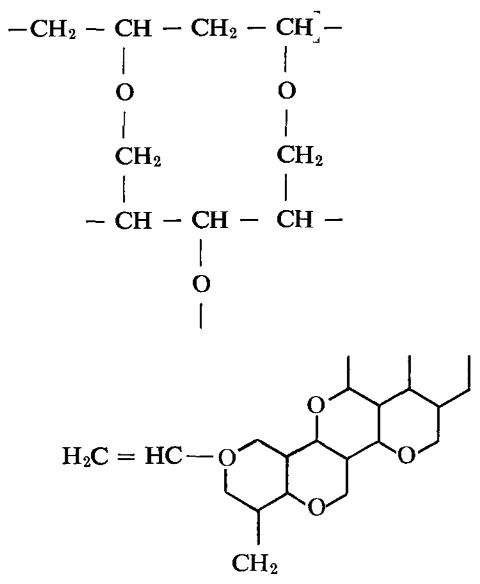


Figure 8 Rate of polymer film deposition as measured by frequency change of quartz crystal oscillator, Δν, for various exposure conditions.

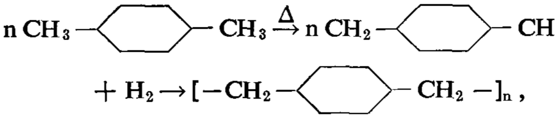
to explain the broad absorption between 8μ and 12μ. Schulz and Wagner have discussed structures for homopolymerized acrolein;[61] the 8–12μ absorption region is attributed to C–O–C bonds:



There is considerable uncertainty concerning the lifetime of free radicals produced on surfaces during ultraviolet photolysis. By using an oscillating crystal microbalance and rotating shutter, Gregor and Hoekstra showed that surface film formation did not occur in the dark after illumination, and that the lifetime of any active surface free radical was less than 10 milliseconds.[62] A typical plot of film growth versus illumination is shown in Fig. 8.

- *Heterogeneous reactions*

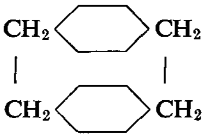
The deposition of polymer films by direct vapor growth from a monomer has usually been avoided because of the inability to form sharply defined geometric patterns on the surface and because the uniformity of thickness, molecular structure, etc. are visible. Recently, it has been reported that polymer films with good dielectric properties can be obtained by allowing a stream of heated p-xylene vapor to impinge on a surface at room temperature. The bulk polymerization of p-xylene to form linear poly-p-xylylene,



(22)

was studied by Swarcz and his co-workers some time ago.[63] In the process developed for film formation, the diradical

is produced by pyrolysis of di-p-xylylene



at 580–620°C; the heated gas stream then strikes a surface at or near room temperature. The diradical combines by a free radical addition mechanism to form the solid polymer films. The dielectric properties of Parylene, the trade name for this material, have been studied by Valley and Wagener.[64]

A more complete description of the physical and electrical properties of various poly-p-xylylene derivatives has recently been given by Cariou, Valley, and Loeb[65] and the chemical aspects of the formation of di-p-xylylene, its pyrolysis, and the recombination polymerization process have been presented by Gorham.[66]

The structure of poly-p-xylylene films has been examined by Niegisch.[67] A transition occurs at 200°C from the α to the β form. Preliminary data indicated that the molecular weight of the film was greater than 200,000, and electron diffraction patterns of the annealed film corresponded to an orthorhombic crystal structure for the α form.

It is of interest to observe that pyrolytic vapor deposition processes, which play a very important role in the production of inorganic dielectric films,[6] are so far of little significance for depositing polymer films. This is due largely to the high temperatures required for pyrolysis which cause intensive carbonization and lead to lower resistivity in polymer films.

Miscellaneous polymer film formation processes

The most straightforward method of forming polymer surface films is to evaporate a substance under vacuum and allow the evaporant to condense on a surface. Whether any particular substance can be converted to vapor or reformed as a polymer is highly dependent on both the structure of the material and the evaporation parameters. This method is most successful for relatively low molecular weight polymers which can evaporate as polymer units and recondense with little or no subsequent reaction. Thin films of polyethylene from 900 to 2500 Å were prepared by White, who employed thermal evaporation of pieces by Polythene sheet in a vacuum evaporator.[68] Using the evaporated film as a capacitor dielectric, he obtained a value of 2.02 for the dielectric constant at 1 kHz. Measurements of tan δ gave a value of the order of 0.015. Another example is the evaporation of Nylon and Teflon.[69,70] Unfortunately, most organic polymers upon heating to temperatures required for evaporation break down into gaseous compounds, which are not reactive and yield a more or less hydrogen-deficient involatile solid. It has been found that thermal evaporation of Teflon results in adherent films only if carried out in the presence of H_2.[70]

The "catalytic" formation of polymer films upon specially prepared surfaces has been proposed as a means of avoiding pinholes.[71] The reaction between gaseous ethylene and an active surface is a possible way to produce polyethylene films.[72] The method is, of course, restricted to coverage of surfaces which are capable of reacting with an ethylene molecule to form a free radical, the film continuing to grow by a chain-reaction addition mechanism until a chain-stopping reaction terminates the process. It is doubtful if such a technique would be of much usefulness unless some method of selectively activating the catalytic surface is available (e.g., electron bombardment of an insulator to create unpaired electrons or ions at predetermined sites).

A very useful polymer dielectric film can be obtained by using a photosensitive material which is coated on a surface and then exposed to light or other form of radiation to convert the substance to an insoluble polymer. Such materials are called photoresists and have been widely used for chemical resists in selective etchings of patterns. Recently, Pritchard and co-workers have studied the dielectric properties of polymerized photoresist films.[73,74] They concluded that polymerized KPR and AZ-17 were suitable as large-area insulators for multilayer film circuits, especially cryogenic circuits.

Thin insulating films may also be deposited on surfaces by the preferential absorption of monolayers of the salts of fatty acids. This technique owes its origins to Langmuir and Blodgett,[75] and has recently been employed by Scale and Handy to prepare extremely thin insulating films.[76] While these films are not truly polymeric, their properties in many ways are similar to those of organic polymers, since the absorbed molecules are essentially long-chain hydrocarbons. The most severe limitations on the use of these films are the limiting thickness attainable (several monolayers) and the low temperature at which the film becomes non-coherent.

Properties of polymer films

Most applications of thin polymer films make use of their dielectric properties. In addition, such factors as chemical and thermal stability, mechanical strength, and interfacial adhesion must be considered in choosing the appropriate material or process. Hence these properties have received most attention in the investigation of such films.

Dielectric properties

Among the most detailed studies of the dielectric properties of polymer films are those on poly-p-xylylene,[64] polybutadiene,[53] polystyrene,[29] and polymethylsiloxane.[39] The detailed dielectric properties of other polymer films have not been reported extensively. Some measurements have been done on polydivinylbenzene (DVB) films deposited by ultraviolet photolysis.[56]

The average dielectric constant of poly-DVB films at 1 kHz and 25°C in air was 3.2 ± 0.4. No published values for bulk poly-DVB are available, but for cross-linked styrene-DVB bulk copolymer, the dielectric constant at 1 kHz is 2.6. The dc breakdown voltage is greater than 1×10^6 volts/cm for films less than 5000 Å thick. Initial reliability of the films, defined as freedom from short circuits immediately after fabrication, was 98% on a test run of 100 capacitors. The dissipation factor, tan δ, varies from 0.002 to 0.005 at room temperature and 1 kHz depending on the film thickness. The dissipation factor decreases slightly with frequency up to 100 kHz. There is a pronounced maximum in the dissipation factor below 100 kHz as temperature is lowered from 25° to −180°C. The broadness of the loss peak increases as frequency is decreased; the center of the peak is about −140°C at 1 kHz. The magnitude of the loss peak increases with increasing film thickness (Fig. 9). The variation of dielectric constant and dissipation factor with temperature is considerably greater for a thick poly-DVB film than for a thin film (Fig. 10). This difference may be due to the fact that the thicker film was prepared at a slightly lower substrate temperature in order to achieve a higher rate of deposition.

In general, the lower the temperature at which the film is formed, the softer the film. The decrease in hardness is due to (a) lower number-average molecular weight, and (b) lesser degree of cross-linking. If such is really the case here, the increase in the degree of temperature-dependent change in K and tan δ with increased film thickness is connected with the increased ease of occurrence of the polarization

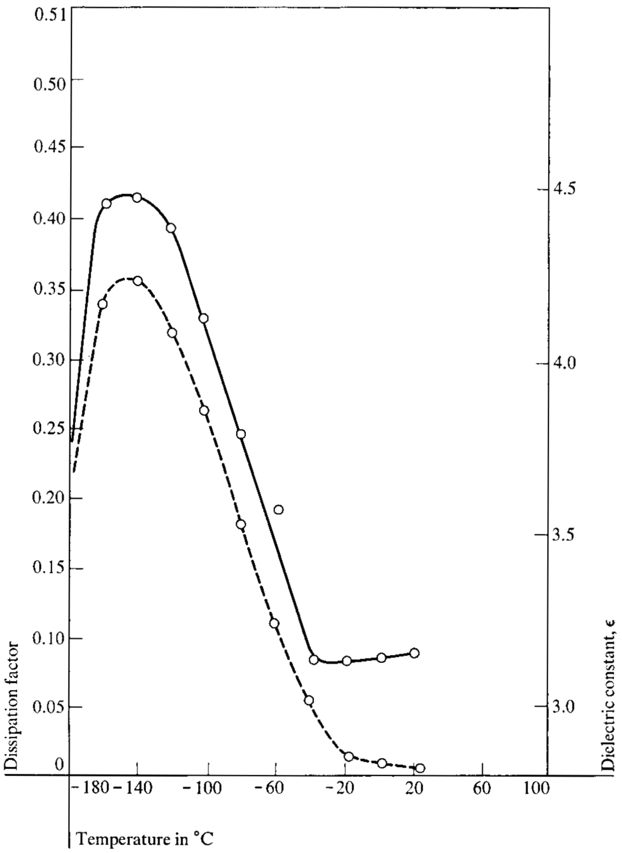


Figure 9 Dissipation factor (solid line) and dielectric constant (dotted line) of polydivinylbenzene film vs. temperature.[56]

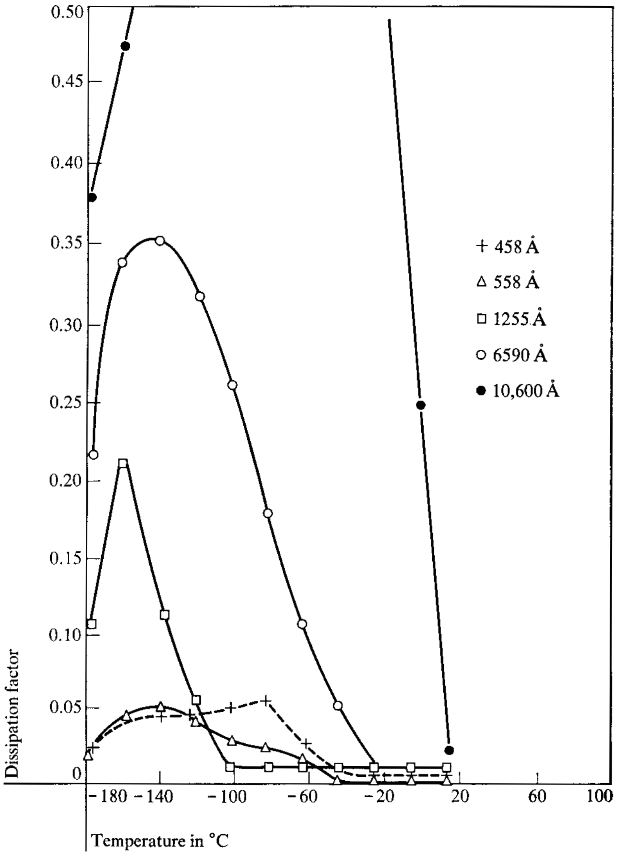


Figure 10 Dissipation factor vs. temperature for polydivinylbenzene films of various thickness.[56]

phenomenon, phase change, or higher-order transition in the film responsible for the energy losses.

A simple dipole relaxation mechanism, which usually accounts for losses at higher frequencies and higher temperatures, should exhibit a marked shift of the loss peak with frequency but not nearly so much with temperature; likewise the effect of lower molecular weight and/or degree of cross-linking should be rather small. This does not fit the observed facts, probably because the dipolar effect is swamped out by the much larger loss peaks actually observed.

No data are available on the heat capacity of cross-linked polystyrene or poly-DVB made from the monomer mixture. The behavior of the thickest films (Fig. 10) which approach bulk dimensions insofar as film thickness compared to chain length is concerned, indicate that such measurements might be of considerable use in determining whether a cooperative transition does occur between −180°C and 20°C. Additional experiments involving the dielectric properties of poly-DVB films which have been irradiated with radiation or bombarded with electrons would also be of interest, since both processes increase the degree of cross-linking and decrease the likelihood of large-scale structure interactions with electric fields.

The dielectric properties of poly-epoxy films prepared by electron bombardment were examined by Jones, who was particularly interested in long term aging effects.[77]

In an effort to characterize the epoxy film, the dielectric properties of a number of thin epoxy film capacitors were measured over a range of frequency 1–64 kHz, and at time intervals following fabrication. Measurements of the capacitance, C, and dissipation factor, D, comprised the data for each specimen; however, the results are most easily discussed in terms of the complex dielectric constant, ϵ^*.

Cole and Cole[78] have proposed an expression which represents the frequency dependence of ϵ^* for a considerable number of materials:

$$\epsilon^* - \epsilon_\infty = \frac{(\epsilon_0 - \epsilon_\infty)}{[1 + (j\omega\tau_0)^{1-\alpha}]}, \tag{23}$$

where

ϵ^* is the complex dielectric constant at any frequency,
ϵ_∞ is the high frequency limit of the dielectric constant,

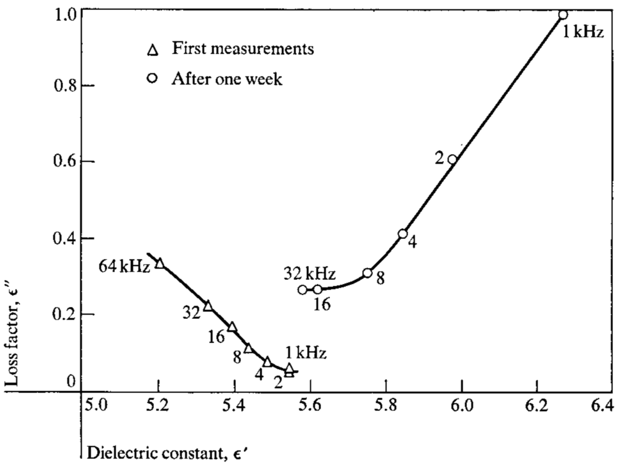


Figure 11 Plot of loss factor ϵ'' vs. dielectric constant ϵ' for poly epoxy films.

ϵ_0 is the low frequency limit of the dielectric constant,
ω is the angular frequency, $2\pi f$,
τ_0 is a characteristic constant called the relaxation time, and
α is a parameter with values between 1 and 0.

If the dielectric specimen in question has two regions of dispersion and absorption, the equivalent circuit will have an additional parallel branch and the equivalent complex dielectric constant for this case will be given by:

$$\epsilon^* = \epsilon_\infty + \frac{A_1}{(j\omega\tau_1)^{1-\alpha_1} + 1} + \frac{A_2}{(j\omega\tau_2)^{1-\alpha_2} + 1}, \tag{24}$$

where

$$\epsilon_\infty = \frac{\epsilon'}{\epsilon_0}, \quad A_1 = \frac{\epsilon_1}{\epsilon_0}, \quad \text{and } A_2 = \frac{\epsilon_2}{\epsilon_0}.$$

The primary interest is in the complex dielectric constant in two frequency regions:

(A) $\omega\tau_1 = 0; \omega\tau_2 \gg 1$.

In this case one has

$$\epsilon^* = \epsilon_\infty + A_1 + A_2(\omega\tau_2)^{(\alpha_2-1)}e^{-(\pi/2)j(1-\alpha_2)}, \tag{25}$$

or

$$\epsilon' = \epsilon_\infty + A_1 + A_2(\omega\tau_2)^{(\alpha_2-1)} \sin(\pi/2)\alpha_2, \tag{26}$$

and

$$\epsilon'' = A_2(\omega\tau_2)^{\alpha_2-1} \cos(\pi/2)\alpha_2, \tag{27}$$

with

$0 < \alpha_2 < 1$, and

(B) $\omega\tau_1 \ll 1; \omega\tau_2 \cong \infty$.

This gives:

$$\epsilon^* = \epsilon_\infty + A_1 + A_1(-j\omega\tau_1)^{1-\alpha_1}, \tag{28}$$

or

$$\epsilon' = \epsilon_\infty + A_1 - A_1(\omega\tau_1)^{1-\alpha_1} \sin(\pi/2)\alpha_1, \tag{29}$$

and

$$\epsilon'' = A_1(\omega\tau_1)^{1-\alpha_1} \cos(\pi/2)\alpha_1, \tag{30}$$

with

$0 < \alpha_1 < 1$.

The plot of the experimentally determined ϵ^* on the complex plane suggested the existence of two dipole relaxations in these dielectrics. Figure 11 is an example of the data which were taken. Initially, the dielectric constant, ϵ', was observed to decrease with increasing frequency while over the same range the loss factor, ϵ'', increased with increasing frequency. These features are consistent with Eqs. (25), (26) and (27) for a dispersion and absorption region peaking at frequencies greater than 64 kHz.

Measurements on the same specimen one week later indicated that a new, low frequency absorption and dispersion had grown in. The real dielectric constant again decreased with increasing frequency; however, the complex component was observed also to decrease with increasing frequency. This is consistent with Eqs. (28), (29) and (30) for a dispersion such that $\omega\tau < 1$ (for frequencies 1 kHz to 64 kHz).

On further analysis it became clear that roughly the same situation existed in every specimen. A high frequency dispersion with approximately the same characteristics was present in all the specimens with a low frequency dispersion superimposed. Furthermore, the amplitude of low frequency resonance in every case increased with elapsed time.

In Figs. 12 and 13, the data for three specimens showing the least evidence of low frequency resonance were fitted to expressions of the form of Eqs. (23) and (24) to obtain the best evidence of the original epoxy characteristics. The average value for the static dielectric constant, $\epsilon_\infty + A_1$, for the original epoxy is 5.02 ± 0.14. The deviations in the figure are most probably due to uncertainty in film thicknesses.

The widely differing parameters α_1 indicate a considerable variation of material properties among the three specimens; however, the values fall in the range to be expected for heterogeneous solids. Unfortunately, there is not a sufficient knowledge of the film structure to indicate the underlying reason for this spread of values.

By estimating A_1, the difference between ϵ^* and the static dielectric constant, an approximate value for the relaxation time τ can be obtained. Assuming A_1 to be 3.5, and using the appropriate values, τ is found to be between 2.5×10^{-8} and 6.8×10^{-8} seconds (6.4 to 2.3 MHz).

The question remains regarding physical or chemical cause of this low frequency dispersion. The epoxy film is porous to the extent that water may be absorbed in cracks or interstices. This absorbed water might be expected to have properties similar to ice. Assuming the dielectric constant of ice ≈ 80 indicates that the total cross sectional area of the "channels" (which effectively act as a capacitor in parallel with the epoxy) to be about 1/40th of the geometrical area of the capacitor. The absorbed layers of water are apt to be small, perhaps 5 Å in thickness. This would require a spacing of about 800 Å between cracks. In following this model the question arises as to why the characteristic relaxation time for this absorbed water is lower than that of ice ($\tau_2 = 1.5 \times 10^{-4}$ sec, observed at 30°K in the epoxy; versus $\tau = 2 \times 10^{-5}$ sec for ice at 0°C). A plausible answer is that the absorbed water is more tightly bound or constrained than in the structure of ice. However, there was no independent confirmation of the presence of H_2O.

In general, detailed dielectric behavior of thin polymer films is extremely dependent on the method of preparation, and the original literature must be consulted and studied carefully to obtain this type of data.

- *Electrical conductivity*

The investigation of electrical conductivity in thin dielectric films has attracted the attention of many workers recently. Most of the experimental work in this field has been done on inorganic films, but some investigations of polymers have been made. As mentioned earlier, the predominant modes of conduction are tunneling, field emission, space charge conduction, and impurity conduction.

A considerable amount of conductivity data for polymer films up to 500 Å in thickness has been presented by Bashara and Doty.[79] In the low temperature range for thinner films the major contribution to current flow may be via tunneling. This has been suggested by Emtage et al.[80] and is illustrated by the zero slope of the log (J/T^2) vs. $1/T$ plot (Fig. 14) for polydivinylbenzene.[27]

The thin film polymer technology is not sufficiently advanced to the stage where thinner films ~50 Å can be fabricated to give short-free devices with a capability of supporting steady current densities in the range of interest. Thus, typically, Schottky emission provides current densities ~10^{-3} amp/cm^2. Since small thin film devices of the order of 10^{-4} cm^2 are desired, the current levels would be $<10^{-6}$ amps. Consequently, this type of current flow is mostly of interest for experimental purposes while tunnel emission is more promising at present for devices.

For narrow barriers there is a significant probability that an electron will be transmitted directly through the barrier by quantum mechanical tunneling. This gives a contribution to the current from all those electrons between the Fermi level and ϕ above the Fermi level in addition to the Schottky emission. In fact, since the density of filled electron states

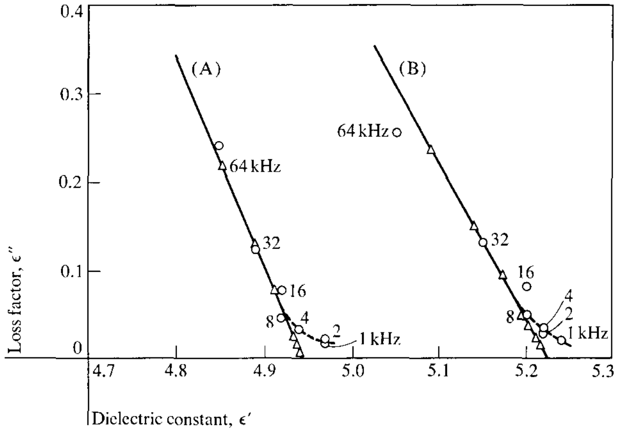


Figure 12 Loss factor vs. dielectric constant for typical poly epoxy films.

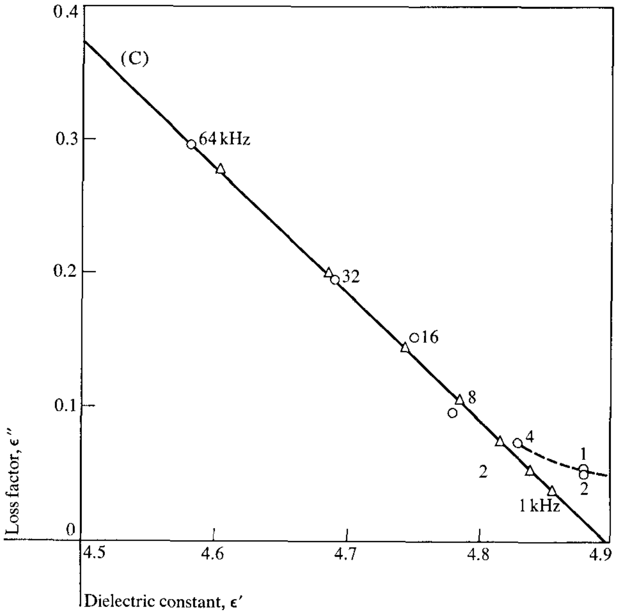


Figure 13 Loss factor vs. dielectric constant for a typical poly epoxy film.

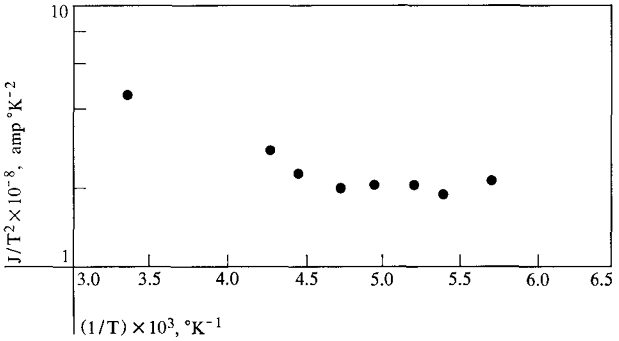


Figure 14 Plot of J/T^2 vs. $1/T$ for polydivinylbenzene film.

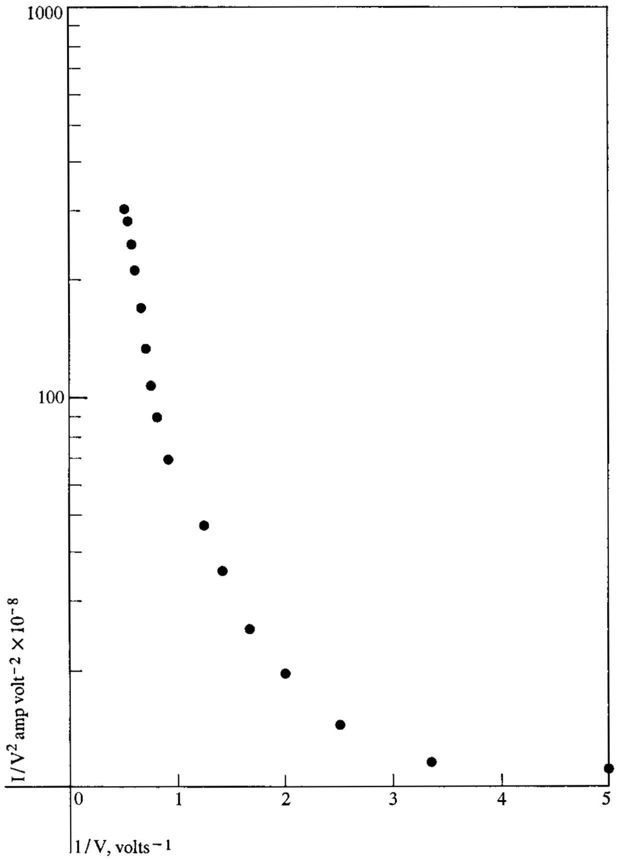


Figure 15 Plot of I/V^2 vs. $1/V$ for polydivinylbenzene film.

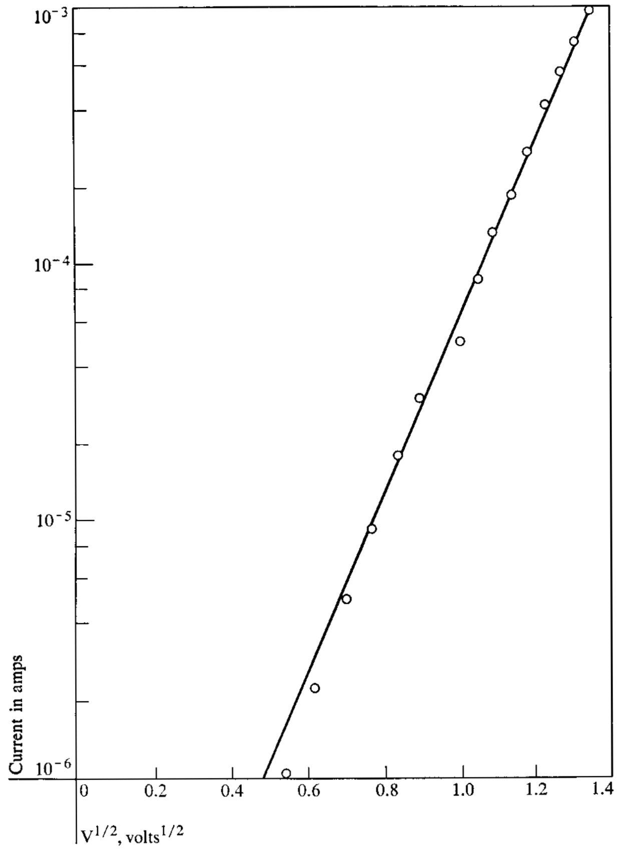


Figure 16 Schottky plot of ln I vs. $V^{1/2}$ for polydivinylbenzene.

falls off rapidly with increasing energy, the contribution from Schottky emission can be quite negligible compared to that from tunneling, provided that the insulating films are thin. Tunneling can be observed at low voltages[81] when log I/V^2 is plotted against the reciprocal voltage, Fig. 15.

Schottky emission in thin films of polymerized silicone oil with Au contacts has been identified by Emtage and Tantraporn.[80] Typical results are also shown for thin films of polydivinylbenzene prepared by a glow discharge technique.[27] In Fig. 16, ln I increases linearly with $V^{1/2}$ as predicted in Eq. (2). The temperature dependence of the current flow for films thicker than 100 Å is also roughly in accord with Eq. (2) provided the temperature is high enough. The constant A determined from the data may be as much as a factor of 10 below the theoretical value and the work function is typically ~0.7 volts for metal polymer contacts.

Stable negative resistance characteristics, which depend on the direction of the applied field, were also observed between 100 Å and 250 Å for polydivinylbenzene.[6,81] The application of a triangular ramp voltage causes a current pulse to appear at 1.2–1.5 volts (rise time ~1 μsec) which then abruptly decreases at 2–3 volts. The negative resistance region is not due to a breakdown of the polymer film, and is strongly dependent on the direction of the previously applied electric field. Thus, the first time a voltage is applied in one direction (A), the negative resistance region is observed. If the voltage is not reversed, all subsequent applications of voltage in direction A show only the Schottky emission current, which becomes significant at 4–5 volts. If, however, the voltage is now applied in the opposite direction (B), the current pulse reappears. This type of symmetrical bistable device is capable of acting as an information storage device. The behavior of such a device for information storage is illustrated by the data shown in Fig. 17. In the first case (arbitrarily taken as state 0), a writing signal of +5 volts is applied to the device; this results in a current pulse when an interrogation signal of −1.5 volts is applied. In the second case (arbitrarily taken as state 1), prior application of a writing signal of −5 volts will result in a current pulse when the device is interrogated at +1.5 volts, or no current pulse at −1.5 volts.

In Figure 17, the sequence begins with the trace labeled 1, in which a positive voltage gives only an emission current at relatively high voltage (>5V). In 2, a reversal of the voltage gives a current pulse at ~ −1.5 volts. Steps

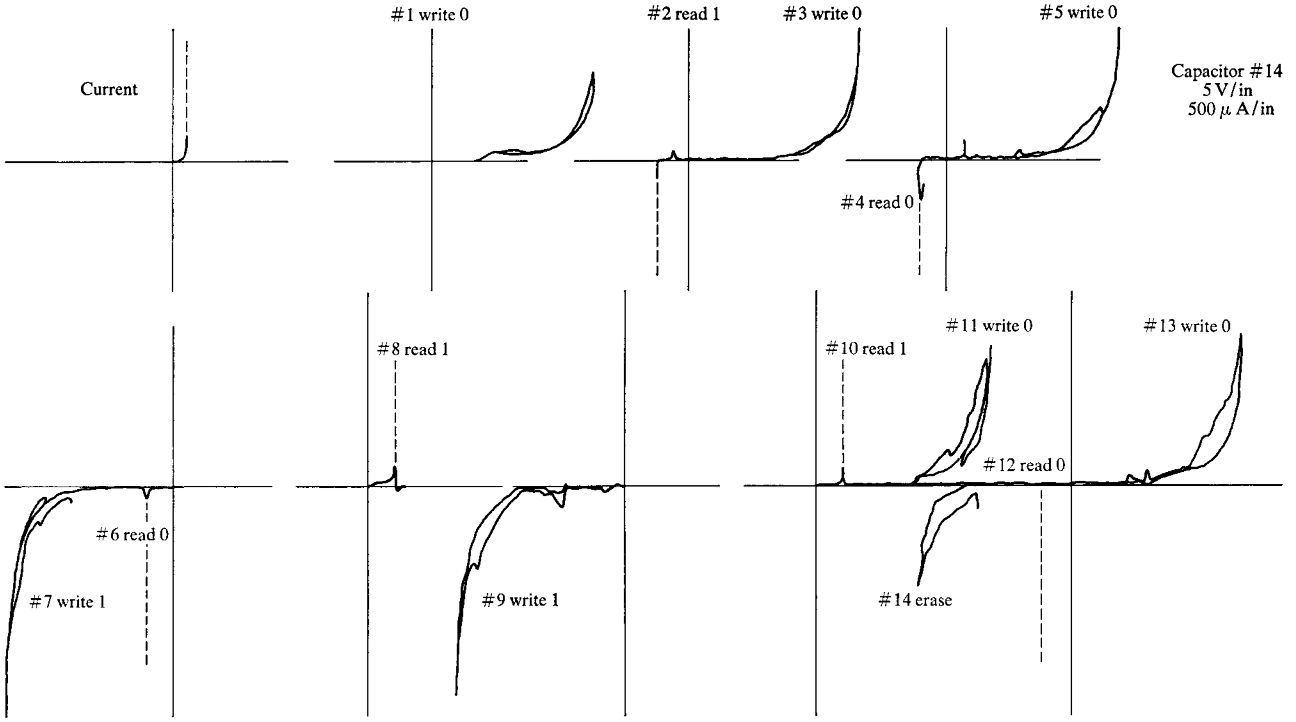


Figure 17 Sequence of *I-V* curves for Pb-polydivinylbenzene-Pb thin film diode showing bistable negative resistance phenomenon used for information storage.

3, 4, and 5 indicate the reproducibility of this state. Step 6 indicates that after interrogating the device, a larger negative voltage can be used to switch to the other state (7). In the other state, a current pulse is now obtained at +1.5 volts (8) and nothing but emission current is sensed with negative voltages. Steps 10 through 13 repeat the switching process. The mechanism of the current pulse is not understood, but appears to be associated with the molecular structures of the polydivinylbenzene film. Somewhat similar negative resistance phenomena were observed for polystyrene films deposited from a glow discharge, but not for polyacrolein or polymethyl methacrylate.[81] It is possible that the electronic structure of the phenyl and phenylene groups are somehow associated with the anomalous conduction, perhaps due to overlapping Π-orbitals.

When dealing with such thin films, it is often necessary to correct the classical capacitance equation because the films are not much thicker than the distance over which image forces are strongly felt. This has been shown by Ku and Ullman,[9] and more recently by Simmons,[82] who has recently published detailed calculations of the magnitude of this effect.

• *Thermal conductivity*

Polymer films are generally poor conductors of heat as well as electricity. An estimate of the thermal conductivity of polymethyl methacrylate in the liquid helium range has been made by Jones, Pennebaker, and Gregor.[83]

The polymer films were deposited on high purity silver substrates by ultraviolet photolysis of a mixture of methyl methacrylate and nitromethane vapors.[54] Just prior to the polymer film formation, the substrates were covered with a layer of evaporated lead several thousand angstroms thick. A similar film was evaporated on top of the polymer film, giving a lead-polymer-lead structure. Contact was made to this structure with indium foil.[84]

The thickness of the 1000 Å polymer films was estimated from measurements on similar films deposited under identical conditions. The thickness of the 3000 Å films is less certain, as it was estimated from interference fringes seen in white light, assuming an index of refraction of 1.87.[54] The error in thickness could be as high as 30%.

Figure 18 shows data taken of two of the six specimens. The unit area thermal resistance is plotted as a function of the polymer film thickness for three temperatures in Fig. 19. The slope of a plot of the unit area thermal resistance w versus thickness d gives the bulk thermal resistivity of the polymer.[84] The intercept gives the apparent contact resistance, which is the sum of the true contact resistance and a thermal resistance in the indium foil used to make the contact. It has been demonstrated that the apparent contact resistance w_c' can be described by[84]

$$w_c' = w_c + BT^{-1}, \tag{31}$$

where

$$w_c = AT^{-3}.$$

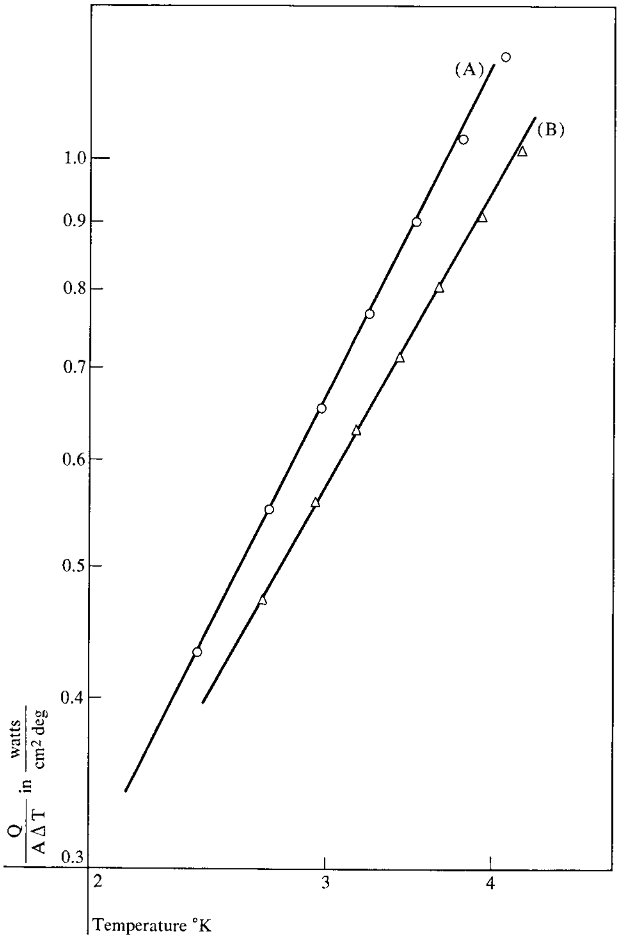


Figure 18 Thermal conductivity of polymethyl methacrylate vs. temperature for two specimens.

Fitting the values of w_c' to this equation, the following values are obtained:

$$A = 9 \pm 2 \text{ cm}^2\text{deg}^4 \text{ watt}^{-1},$$
$$B = 0.75 \text{ cm}^2\text{deg}^2 \text{ watt}^{-1}.$$

The error estimate in A is obtained from the range of straight lines compatible with the error flags in Fig. 19. The value of B is quite consistent with those found previously for silicon monoxide films (0.75 to 1.20 cm^2 deg^2 watt^{-1}),[84] adding support to the hypothesis that this part of the thermal resistance arises in the indium foil used to make the contact.

The bulk thermal resistivity w_i of the polymer, obtained from the thickness dependence of the thermal contact resistance is given in Table 4. w_i varies approximately as T^{-1}, indicating that "intrinsic structure scattering"[84] is the dominant scattering mechanism. The magnitude of the thermal resistivity is a factor of 10 larger than the resistivities of glass,[84] indicating either that the correction length is shorter in this polymer than in glass or that the variation in elastic constants is greater in the polymer.[85] Both the thickness of the film and the phonon wavelength must be greater than the correlation length if the thermal resistivity is to vary inversely with temperature. This means that the correlation length must be somewhat smaller than the dominant phonon wavelengths of approximately 200 Å (at 4°K). If it is assumed that the correlation length is of the order of the average molecular chain length, this length cannot be much larger than 100 Å. This would mean an average nonbranched chain of about 15 monomer units (assuming a monomer length of 6.7 Å).

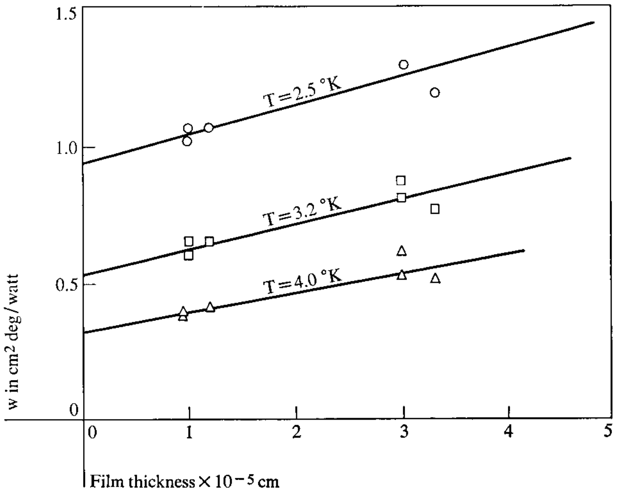


Figure 19 Unit area thermal resistance of polymethyl methacrylate vs. thickness at three temperatures.

It is possible that the chain length is considerably shorter than 100 Å for these polymer films. It has been observed[56] that the dielectric constant of polydivinylbenzene films is considerably different from films quenched to liquid nitrogen temperature than for films cooled slowly. Polydivinylbenzene is quite similar to the polymer used for this study. The difference between quenched and slowly cooled films is evidence of a slow ordering taking place at about −80°C (where by hypothesis kT is about equal to the energy needed for rotation of segments of the polymer chain). Since the poly (methyl methacrylate) films used for these thermal resistance measurements were rapidly cooled to liquid nitrogen temperature, the room temperature disorder is probably frozen in. Having established the amorphous character of the polymer, one can proceed to a calculation of the thermal contact resistance. It is again necessary to assume that the transverse modes are strongly scattered in the polymer and do not contribute to the heat current. The close resemblance to lucite of the polymer in these films makes it reasonable to use the measured sound speed and density of lucite in the calculation. Thus, the values $v = 2.7 \times 10^5$ cm/sec and $d = 1.18$ gm/cm^3 are used to find $A = W_cT^3$:

$A = 7.4$ cm^2 deg^4 watt^{-1}; phonon radiation model.
$A = 15$ cm^2 deg^4 watt^{-1}; acoustic impedance matching model.

The experimental value $A = 9 \pm 2$ cm^2 deg^4 watt^{-1} seems to favor the phonon radiation model. It should be remembered, however, that a considerable error in the calculated values may arise from the assumption that the polymer has the same sound speed as lucite. In either case, polymer films are poor thermal conductors. However, since polymer insulating films are thin, the temperature gradient across a film is usually small. For example, one can estimate the temperature difference ΔT caused by evaporation of a metallic film onto a previously deposited polymer film. Choosing Pb as the metal and polymethyl methacrylate as the polymer, an approximate calculation can be made of the temperature difference across a film 0.1μ thick, assuming that only the heat of sublimation of the Pb film contributes to the temperature rise. This turns out to be 0.0023°C.[87] Radiation from the source will probably be much more important in determining ΔT.

• *Chemical properties*

The rich variety of molecular structure found in polymer films leads to a broad scope of physical and chemical behavior. In fact, it is necessary to consider each particular polymer film individually in order to discuss chemical behavior. Such a task is clearly beyond the scope of this work, but a few examples will be given to indicate the general principles.

In general, the properties of polymer films are determined primarily by the deposition process and secondarily by the monomer or starting material. For example, divinylbenzene forms a polymer film upon exposure to ultraviolet irradiation which is soluble in acetone and softens when heated above 120°C. This is in accordance with a structure obtained by vinyl addition polymerization at one double bond. Also, the film would probably be attacked by oxygen, the halogens, and the hydrohalides at the remaining double bond. However, if divinylbenzene is polymerized by electron bombardment or in a glow discharge, a tough solvent-resistant film is formed due to cross-linking.

Another example is poly-p-xylylene. When unsubstituted p-xylene is used as the starting material the polymer film obtained (Parylene N) has characteristic transmission coefficients for penetration by various gases. If chloro-p-xylene is the original substance, these permeabilities are considerably different. Presumably, substitution of more halogen atoms would lead to a more oxidation-resistant film.

The highest degree of chemical inertness and thermal stability can probably be achieved by fluorocarbon polymer films, although very little information is available concerning such films. Increased thermal stability is also to be expected for polyaromatic hydrocarbon polymers.

• *Mechanical properties*

Measurements of residual stress in deposited polymer films are scanty. Using the technique of Priest, Caswell and Budo, the residual stress in epoxy polymer films deposited by electron bombardment was not detectable, setting an upper limit of 10^8 dyne cm.[88] This affords a considerable improvement over most thermally evaporated dielectric materials. For example, the residual stress found for evaporated silicon monoxide films may be as high as 10^9 dyne cm.[89]

Other mechanical properties, such as hardness, tensile strength, elastic limit, etc., have not been reported, perhaps because of the difficulty of performing and interpreting experiments which would yield such information on such thin, supported films. In general, films produced by ultraviolet photolysis are softer than other types, and impact deformation is usually plastic. These films are relatively poor in abrasion resistance, and may be cut or ruptured easily by a sharp point. Considerable data on mechanical and other engineering properties have been published for poly-p-xylylene films.[90]

Applications of polymer films

The polymer film deposition processes previously discussed are not susceptible to simple intercomparison. That is, one cannot state that a particular process is "best" without carefully considering the requirements to be met.

At the present time, the most practical polymer film process is the glow discharge method. This process gives conformal coatings, can be adapted to continuous processing, and has applications beyond electronic insulation. The major drawbacks encountered are the lack of precise control of film composition and the difficulty of producing high resolution film patterns. Essentially the same can be said of the vapor phase deposition of the various polymers derived from p-xylene, although better compositional control can be achieved.

The other film deposition techniques offer particular advantages in structural specificity, high geometric definition, and reliability at exceedingly small thicknesses. In particular, the use of electron bombardment appears to have considerable potential application for deposition of thin film insulation for microelectronic applications.

The direction of future developments in polymer dielectric film technology appears to lie in increasing both the thermal stability and long-term electrical reliability of such films. Recent advances have been made in producing heat-resistant bulk polymers by synthesizing highly conjugated

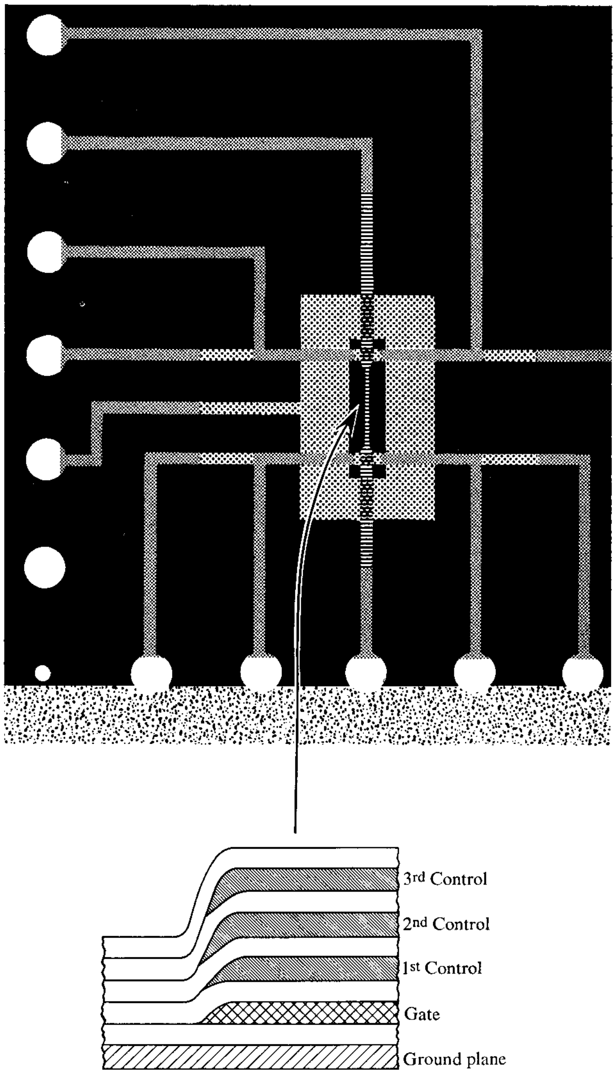


Figure 20 Typical superconducting cryotron switching element.[88]

polymer structures, and this may prove to be fruitful if such structures can be synthesized as thin films. Chemical stability may be improved by incorporating "inorganic" molecular units into the polymer structure; however, there is generally a trade-off between the desirable "plastic" properties of organic polymers and the chemical stability but brittle mechanical properties of inorganic materials (glasses, crystalline films, ceramics).

Thin dielectric films find their most useful potential employment in the fabrication of thin-film, hybrid, and monolithic integrated electronic circuits. This will be true no matter what direction future developments take. At present, the most promising type of microelectronic circuit is the monolithic silicon integrated circuit. The usefulness of silicon monolithics would be greatly enhanced if a more reliable thin-film dielectric can be developed for insulating the various levels of metallic interconnecting films from each other. The current practice is to utilize SiO_2 or glass films deposited by sputtering, pyrolysis, or direct application and firing. While these films are chemically stable and resistant to high temperatures, they are also very brittle and may be subject to severe stress buildup. This is where the polymer films possesses certain advantages, because of the polymer ability to undergo plastic deformation in response to stresses.

The use of polymer insulating films directly on semiconductor surfaces to supplement or replace the conventional oxide and glass films does not appear feasible in most cases because of the high temperatures employed in metallization and sintering. Polymer films have been used for experimental measurements of the surface potential and surface state density of silicon.[91]

The most important application of thin polymer dielectrics at present is in the production of capacitors, particularly in applications where a high capacitance per unit area (or unit volume) is desired. Two processes are particularly attractive for this purpose: the gas discharge and pyrolytic techniques. Both can be adapted to continuous coating of a metallic foil with a uniform polymer film. The foil is then rolled into a capacitor with an extremely large capacitance/volume ratio. Extensive descriptions of the properties of such capacitors have been given by Cariou, et al., for Parylene,[65] and by Goodman, et al. for glow-discharge polymer films.[92]

Another promising area for application of polymer dielectric films is in the fabrication of cryogenic thin-film circuits. The insulation requirements are particularly stringent in this case, since the dielectric layer must be very thin and uniform, and yet must withstand the stress imposed by differential thermal contraction upon cooling to the temperature of the cryogenic system, about 3°K. Among the polymer films which have been used for cryotron insulation are polymerized photoresist,[73] poly-epoxy films made by electron bombardment,[45] polymer films from various vacuum pump oils by the same method,[48] and poly-p-xylylene.[87] A typical cryotron circuit using poly epoxy insulation is shown in Fig. 20.

An important requirement for the practical use of polymer films in cryogenic circuit applications is that the polymer film pattern must be capable of selective deposition to a high degree of resolution. A desirable, though not necessary, feature is that the deposition process be compatible with the vacuum evaporation techniques and vacuum chamber equipment used for the deposition of the metallic film elements of the circuit.

Films of polybutyle methacrylate have been deposited by ultraviolet photolysis using an evaporation mask, and subsequently employed as resist films for subtractive etching of an underlying metal film. Because of the non-crosslinking nature of the photolytic process, the resist films were then easily removed by dissolution in a solvent such as acetone.[93]

Films of Parylene have been used as the gate insulation in silicon field effect transistors with some success. After diffusing in the source and drain regions, the oxide diffusion mask was removed and Parylene deposited over the surface. By employing a special photoetching technique, contacts were opened to the silicon, and then aluminum was deposited and subsequently subtractively etched to form the gate electrode and contacts.[94] No quantitative results have been reported concerning the operation of the devices or the stability.

The thin-film field-effect transistor, or TFT, is another experimental device which requires a thin insulating film between the gate electrode and the semiconductor channel. Since the insulating layer cannot be grown as it is for silicon FET devices, a deposition method is necessary. Polymer dielectric films may find an application in this type of device, provided they possess stable properties at high electric fields.

Some highly exploratory work has been done to utilize the conduction mechanisms of very thin polymer films for fabrication of novel thin film active devices such as hot-electron triodes, tunnel devices and negative resistance elements. Although no practical devices have yet been demonstrated, it is by no means clear that they will not be, once materials and techniques reach the appropriate state of development. The potential advantages of such devices as a tunnel triode are the small size and absence of temperature dependence of the tunnel current.

The non-ohmic conductivity of thin polymer films has been utilized in an active thin film device by Schmidlin. He claimed that a thin polymer film, up to 300 Å, between two layers of heavily-doped semiconducting material produced a device with negative resistance characteristics.[95] Likewise, a thin film of organic insulation was claimed by Davis to enable him to fabricate active thin film electronic devices based on electron tunnelling through the polymer insulation barrier.[96] Thin self-supported polymer films have been employed as radiation filters and particle detectors. In particular, films of poly-p-xylylene are suited for this purpose because they can be deposited by appropriate techniques and stripped from the substrate.[97]

Very thin polymer dielectric films may prove to be useful in fundamental investigations of the behavior of certain systems in very strong electric fields. An example is the study of the Stark effect on the electronic energy levels of certain organic molecules such as dyes.[98] Such an effect can cause a shift in the absorption spectrum of the dye and hence a color change, but the effect is not large until fields in excess of 10^6 V/cm are obtained. By incorporating the chromophoric group into the molecular structure of a polymer dielectric film, such investigations could be carried out with much less experimental difficulty.

Recently, it has been found that coatings of certain materials such as cholesterol benzoate undergo color changes due to localized heating. These materials have been used to detect "hot spots" on integrated circuits and are useful for analysis of power dissipation in tiny complex semiconductor arrays.[99]

Finally, by enabling the research worker to investigate electrical conduction in very widely varied organic materials, the use of thin polymer films may help to unravel some of the mechanisms of electrical conduction in biological systems, and perhaps to find some relationship with metallic conductivity. It has been proposed that certain types of highly conjugated polymer systems may be capable of exhibiting the phenomenon of superconductivity at temperatures much higher than any known metallic or compound superconductor.[100] The possibility of synthesizing such polymers may lie in some of the thin-film approaches now available as a result of the investigations discussed above.

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