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PRODUCTION OF ORGANIC SURFACE FILMS BY THE ACTION OF ELECTRONS, ULTRAVIOLET RADIATION, AND THE GLOW DISCHARGE

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I. INTRODUCTION

The production of polymeric products on solid surfaces, by the action of electron bombardment or ultraviolet radiation on organic compounds of low molecular weight, or in the glow discharge, is of interest both from the theoretical point of view and in connection with the practical utilisation of this effect. Under these conditions films can be obtained from practically any organic compound, whereas with ordinary methods of polymerisation or polycondensation the presence of unsaturated bonds, rings, or certain functional groups in the molecules is essential. It is an extremely complicated task to establish the mechanism of the chemical reactions caused by the action of active particles on an adsorbed layer and leading to the formation of polymer films on the surface. It must be borne in mind that the resulting polymer is also subject to the action of ions and electrons, which may produce free macroradicals and cause degradation and cross-linking reactions. In view of the complexity and diversity of the reactions occurring under these conditions and leading to the formation of polymer films, only qualitative assessments can at present be made of their mechanism.

The method under discussion has already found practical application for the production of insulating and anticorrosive coatings. The thin polymeric films obtained in this way on a solid surface are distinguished by high thermal stability, chemical stability towards acids, alkalis, and organic solvents, good adhesion, and also homogeneity and the absence of pores. These properties of films, their superior dielectric characteristics, and the possibility of obtaining films of semiconductor type under special conditions indicate the wide opportunities for applying the method in various technical fields, and especially in microelectronics.

The present review will examine successively the possibilities and conditions for obtaining polymer films on solid surfaces by electron bombardment, in the flow discharge, and under the influence of ultraviolet radiation. Problems connected with possible practical uses of this method will be discussed separately.

II. PRODUCTION OF POLYMER FILMS ON IRRADIATION OF A SOLID SURFACE WITH ELECTRONS

Formation of polymeric films on solid surfaces under the influence of electrons occurs even with low concentrations of the organic substance in the gas phase, corresponding to pressures of 10^{-4} mmHg or lower. Consequently the processes governing film growth take place mainly in an adsorbed layer, since the probability of interaction between electrons and molecules in the gas phase is extremely small at such low pressures. Interaction between electrons and sorbed molecules may lead to a diminution in the concentration of molecules in the adsorbed layer or to the formation of polymeric deposits on sites which have been subjected to electron bombardment.

The qualitative view held at present on the mechanism of these processes is that desorption of molecules into the gas phase can take place only by inelastic collisions of electrons with the molecules: otherwise, the transfer of kinetic energy is too small to detach the molecules from the surface. In inelastic collisions, electronic states in the sorbed molecules can be excited, which may lead to dissociation of the molecules into fragments (ions and radicals). The fragments, which possess sufficient kinetic energy to overcome the bonding to the surface, are desorbed. Those fragments which have not acquired sufficient kinetic energy on dissociation remain on the surface, and may react either with one another or with molecules of the starting material, which will lead to the formation of solid polymeric deposits on the surface. Hence it follows that the interaction of electrons with sorbed organic molecules may lead simultaneously to the desorption of particles into the gas phase and to the formation of polymeric deposits on the surface. Henceforward we shall examine only one aspect of this process—the deposition of polymer films.

It must be mentioned, however, that very intensive research is now being undertaken into processes of the desorption of molecules under the influence of electrons. This is of definite interest for an understanding of the processes occurring in heterogeneous catalysis, and for radiation-chemical reactions on a solid surface. The investigations have shown (1) that the probability of desorption of molecules under the action of electrons is small[1]—from 10^{-3} to 10^{-5}—while the desorption of positive ions is still less probable[2], whereas the probability that molecules will be desorbed by ions approaches unity[3]. (2) The appearance potentials of ions from adsorbed molecules are lower than those of the same ions from molecules in the gas phase. This suggests that adsorption considerably changes the energy state of the adsorbed molecules in comparison with their state in the gas phase[1,4]. (3) Curves for desorption plotted against the energy of the electrons pass through maxima, whose positions agree well in most cases with the excitation functions of the molecules in the gas phase[5]. These results confirm that desorption is caused by dissociation of excited molecules and ions into neutral and charged species. (4) With electrons of low energy ($E < 6$ eV) the desorbed molecules do not differ in character from the initial molecules, which probably indicates that in this case

desorption is due to simple dissociation of complexes formed by the sorbed molecules with atoms of the support[6].

It is possible[7-9] to prepare graft polymer layers on various inorganic surfaces by exposing the latter to fast electrons (700 kV and more) in the presence of gaseous monomers. However, the conditions under which polymerisation takes place in this case (highly penetrating radiation, high vapour pressure of the monomer) are fundamentally different from those adopted in work on the action of electron bombardment, and therefore these results will not be discussed here.

1. Influence of Various Factors on Rate of Formation of Polymer Films by Electron Bombardment

The deposition of polymeric coatings on surfaces exposed to electrons in a vacuum was discovered as long ago as the 1930s. Stewart[10] observed the formation of insulating deposits when metallic substrates were bombarded with electron and ion beams. The electrical resistance of the films was measured as well as the breakdown voltage, and the films were also shown to be thermostable up to 450°C.

Further development of work on these lines resulted mainly from observations made when various specimens were examined in the electron microscope. It was found that, under the conditions of exposure in such an instrument, the specimens in time became covered with a brown coating and changed in size. This phenomenon was noted by many workers[11-14]. König and Winkler[15,16] observed the formation of carbon when specimens of organic origin were examined in the electron microscope. Cosslett[17] observed the formation of polymeric deposits on specimens of the oxides of nickel, molybdenum, and magnesium.

One of the first to make a special investigation of this phenomenon was Watson[18], who measured the size of carbon black particles in an electron microscope. He discovered that the particles increase in size with time owing to the formation on them of a light brown film. He suggested that the film resulted from the action of the electron beam on the vapours of organic substances.

Hillier[19] investigated the chemical properties of the film and the kinetics of its growth as a function of various factors. He showed that the film was insoluble in the usual organic solvents, strong acids, and alkalis, has an amorphous structure, and always contained carbon. The rate of film growth was proportional to the first power of the intensity of irradiation, did not depend on the material of the substrate, and fell with time. If, however, irradiation was terminated after a certain time, and was then begun again, the rate of growth reached its original value. This was explained[19] by a low rate at which the surface layer was filled with molecules. Hillier concluded that film formation occurs only when three factors—a vapour capable of yielding a polymer, a surface on which it can be formed, and a beam of electrons—are present. It was assumed that the surface was activated by the irradiation, and behaved as a catalyst. The organic molecules could reach the gas phase in two possible ways—by spontaneous diffusion from metal gaskets, the walls, and grease, and by degassing of metal parts of the instrument under the influence of electron bombardment. To prevent film formation this author recommends first eliminating the access of organic substances to the gas phase.

Ennos[20] used a specially designed apparatus to investigate the cause of the deposition of films on solid surfaces and methods for their elimination. Direct measurements of film thickness established that the films grow at a rate of 1 Å s^{-1} with a current density of 0.5 mA cm^{-2}, electrons of energy 40–75 keV, and a pressure of 10^{-5} mmHg. He showed[20] that the rate of growth of the film is independent of the duration of exposure or the energy of the electrons within the above range, although it is strongly dependent on the temperature of the substrate. Discussing the mechanism of film formation, this author concluded that the deposits were formed by the interaction of organic molecules with the electron beam on the surface of the substrate, where a considerable concentration of hydrocarbon molecules is produced by adsorption. This same view on the mechanism of the formation of polymeric deposits was held also by Poole[21], who emphasised that, even with the organic substances at pressures of 10^{-4} mmHg and above, all processes responsible for film formation take place on the surface, not in the gas phase.

Several suggestions had been made even earlier to explain this phenomenon. Watson[18] assumed that film formation was due to ions produced in the residual atmosphere and deposited on the support near the electrically conducting surface. However, an estimate of the deposition due to ions formed in residual gases gives values for the reaction velocity which are smaller by several powers of ten than those observed experimentally.

Cosslett[17] supposed that film formation was due to ejection of adsorbed substance, perhaps of metal itself from the grid of the specimen-holder, on electron bombardment.

Haefer[22] noted that deposition of a substance on a substrate may result not only from the reactions of electrons and ions with adsorbed molecules but also from cathode sputtering. Ellis[23], like most workers, considered that a film was formed as a result of resinification of organic substances under the influence of the electron beam, but differed in ascribing replenishment of the number of adsorbed molecules mainly to the migration of molecules on the surface, while replenishment from the gas phase was of considerably less importance. However, Ennos[20], on the basis of the experimental results, reached the opposite conclusion—that replenishment of the number of adsorbed molecules by surface migration played an insignificant part in comparison with that from the gas phase.

Thus study of the reasons for contamination of specimens in an electron microscope and elucidation of the conditions under which it would be minimised have led to establishment of the important fact that the formation of polymeric deposits results from interaction of electrons with molecules in the surface layer.

In later work, where experiments have been made both in specially designed apparatus and in electron microscopes, the kinetics of film formation and the factors influencing the rate of growth have been studied quantitatively and in greater detail. The experimental techniques have been described in detail in the original papers, so that they will merely be mentioned here. Film thickness has been determined interferometrically[24,25], by means of a piezoelectric crystal[26], and by weighing[27]. Films of a sputtered metal[28,29] and of a dielectric[25] (quartz, glass) were employed as substrates. Experiments were made mainly in an atmosphere of the vapours of certain organic substances, but in some work use was made of an atmosphere of the residual gases in vacuum equipment, which always contain hydrocarbons.

The relative abilities of various organic substances to contaminate vacuum equipment was studied[30] by introducing them into a clean vacuum system, and then determining the characteristics of the polymeric deposits formed on surfaces bombarded by electrons. The tendency to film formation diminished in the sequence—hydrocarbon oil of diffusion pumps, vacuum greases, various types of rubber gaskets, silicone oil, and vacuum wax. Experiments carried out at the same time on the temperature dependence of the rate of deposition showed that raising the temperature to 200°C reduced the rate of film growth to 10% of its previous value. A cold trap at −15°C has a similar effect.

The influence of the temperature of the substrate on the rate of film formation on the surface has been investigated for various organic compounds[20,24,26,30-34]. Leisegang and Schott[32] studied the effect of temperature on the rate of contamination of a specimen in an electron microscope, and found the rate to diminish with rise in temperature. Christy[25] studied the rate of formation of films from the silicone oil DS 704 as a function of the current density of electrons with the substrate at various temperatures, and confirmed that rise in temperature diminishes the rate of film growth. Haller and White[26] studied the dependence of the rate of polymerisation of butadiene on its pressure in the gas phase (over the range 10^{-6}–3×10^{-4} mmHg), and established that the rate diminishes with rise in temperature throughout the pressure range investigated.

Several investigations have been made of the influence of the nature of the substrate on the rate of formation of polymeric deposits[19,21,35]. Experiments with silver, steel, copper, nickel, and copper–nickel alloy substrates revealed no dependence of rate of film growth on substrate material[21]. This is confirmed by the results of other work[19]. A study of film formation on nickel, copper, platinum, silver, iron, glass, and crystalline sodium chloride substrates in an electron microscope[35] yielded no definite conclusions on the influence of the substrate on the rate of film formation. The fact that no such relationship was observed in the above work is probably due to a phenomenon subsequently discovered by Mann[36], who studied the secondary electron emission from polymeric films under the influence of an electron beam. He found that, up to a film thickness of 25 Å, secondary emission occurs simultaneously from the growing film and from the substrate, whereas with thicker films secondary emission is observed only from the growing films themselves. It was shown that, with the substrate at a positive potential relative to the electrode accelerating the electron beam (which is usually the case in all experiments), secondary electrons also play a definite part in film formation. It may be concluded from this work that the material of the substrate can influence the rate of film growth only in the early stages of the process.

The influence of the vapour pressure of organic substances has been investigated[25-27,37]. Haller and White[26] determined the dependence of the rate of film growth on the pressure of butadiene over the range 1.3×10^{-6}–3.2×10^{-4} mmHg, and found the rate to increase with rise in pressure only to a certain limit, this saturation occurring at higher pressures with greater electron currents (Fig. 1). Similar pressure effects have been observed[27] in an investigation of the behaviour of silicone oil, and also in other work[19,25]. In another piece of work[37] the rate of film growth was found to be independent of the pressure of butadiene. This was probably because these experiments were conducted at high pressures, at which the rate had ceased to depend on pressure.

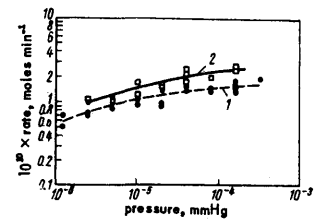


Fig. 1. Pressure dependence of rate of polymerisation of butadiene at: 1) 400 μA; 2) 800 μA.

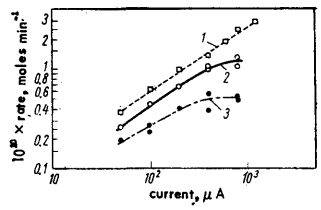


Fig. 2. Dependence of rate of polymerisation of butadiene on the current at pressures of (mmHg): 1) 1.6×10^{-4}; 2) 4.0×10^{-5}; 3) 1.3×10^{-5}.

The influence of the current density of the electron beam on the rate of film formation has been investigated[19,24-26,32]. Christy[24] found that, with a silicone oil, the relation is non-linear, the rate reaching saturation at definite values of the current. Haller and White[26] showed the rate of film formation from butadiene to be proportional to the square root of the current density. At higher currents the curves tend to form a plateau, this occurring at higher current densities the higher the pressure (Fig. 2). Similar results for the influence of current density on rate of film formation were obtained by other workers[32], and also more recently[38,39].

No detailed study has yet been made of the dependence of the rate of film growth on the electron energy. Only isolated experiments have been made, and in these the relationship was investigated only over a narrow energy range. Thus the rate at constant current density and pressure has been found[20] not to depend on the energy of the electrons over the range 40–75 keV. Nor does variation over the range 200–600 eV influence the rate of film formation from silicone oil[27]. Mayer[38] made experiments in a reflecting electron microscope, and found the rate to increase with low electron energies over the range 6–25 eV.

The influence of the duration of irradiation on the rate of formation of films has been examined[20,24,26,27,38]. Over the times investigated the rate was found to be independent of duration. A constant rate of growth is maintained[24,27] for film thicknesses of several thousand Ångström units.

It has been shown[24,40] that films of either semiconductor or metallic type can be obtained by irradiating solid surfaces with electrons in an atmosphere of the vapour of an organometallic compound [or of an inorganic salt of the tin(II) chloride type]. Baker and Morris[40] have demonstrated that, under more severe experimental conditions

(electrons of energy up to 1 keV, current density of ~ 5 mA cm^{-2}), the decomposition of the vapours of organometallic compounds (tetrabutyltin, tetramethyltin, tetraethyl-lead) proceeds as far as formation of a film of the pure metal on the surface of the substrate. Decomposition of tetrabutyltin $(C_4H_9)_4Sn$ on a quartz surface yields [25] films not of pure tin but of polybutyltin, possessing semiconductor properties. Both the rate of growth and the composition of the films depend on the pressure of tetrabutyltin vapour in the gas phase, the current density, and the temperature of the substrate. The same work included an examination of the formation of tin films by the decomposition of tin(II) chloride molecules by electrons on a quartz substrate.

2. Mechanism of Formation of Polymer Films

Most research workers consider that film formation is due to processes occurring in the surface layer as a result of interaction between sorbed molecules and electrons. The mechanism of film formation has been discussed in greater detail [24,26,37,41]. The process is supposed to occur in two stages: (1) active centres (radicals and ions) are formed on the surface by interaction of electrons with sorbed molecules; and (2) sorbed molecules react with these active centres. The surface formation of polybutadiene films, in particular, has been interpreted in this way [26,37,41]. These authors consider that the polymerisation of butadiene proceeds initially on the surface of the substrate, and continues as the film grows by interaction of adsorbed gas molecules with active centres of the polymer surface.

There is no generally accepted view in the literature as to whether ions or radicals play the main part in the process. Several workers assume a radical mechanism. This conclusion was reached by Christy [24], who examined the behaviour of silicone oil, and found that polymer formation results from the recombination of free radicals produced by the action of electrons on adsorbed molecules. Haller and White [26] supply evidence that the surface polymerisation of butadiene proceeds by an ionic mechanism. It is most likely that both mechanisms of polymerisation may play a part in film formation, with one or the other predominating depending on the experimental conditions and the nature of the molecules of the starting material. Schemes have been discussed [26] for both mechanisms applied to the polymerisation of butadiene on the surface of an already formed film.

The radical mechanism of polymerisation can be represented by the equations

$$P + e \rightarrow P^{\cdot} + H^{\cdot} + e \quad k_1 I \tag{1}$$

$$P^{\cdot}_M + Bu_a \rightarrow P^{\cdot}_{M+1} \quad k_2 [P^{\cdot}]\ [Bu_a] \tag{2}$$

$$P^{\cdot}_M + P^{\cdot}_N \rightarrow P_{M+N} \quad k_3 [P^{\cdot}]^2 \tag{3}$$

where P is a polymer molecule, Bu_a is an adsorbed butadiene molecule, P_M and P_N are polymer molecules on the surface containing respectively M and N monomer units, and k_1, k_2, and k_3 are the rate constants of reactions (1)–(3) respectively. On the assumption that the size of a radical does not affect its chemical properties and that the concentration of adsorbed monomer is constant, the rate of polymerisation can be written

$$r = -\frac{d[Bu_a]}{dt} = k_2 \sqrt{\frac{k_1}{k_3}} I [Bu_a]. \tag{A}$$

The relation between the pressure of butadiene in the gas phase and the surface concentration of its molecules $[Bu_a]$ is determined by the adsorption isotherm.

The ionic mechanism of polymerisation is described by the equations [26]

$$P + e \rightarrow P^{+} + H^{\cdot} + 2e \quad k_4 I \tag{4}$$

$$P^{+}_M + Bu_a \rightarrow P^{+}_{M+1} \quad k_5 [P^{+}] [Bu_a] \tag{5}$$

$$P^{+} + e \rightarrow P \quad k_6 [P^{+}] I \tag{6}$$

$$P^{+} + e_c \rightarrow P \quad k_7 [P^{+}] [e_c] \tag{7}$$

$$e_c + s \rightarrow e_s \quad k_8 [e_c] \frac{dv}{dx} \tag{8}$$

$$e_c + L \rightleftarrows e_L \quad [e_c] = [e_L] \exp(-E_L/kT) \tag{9}$$

where P is a polymer molecule, P^{+} a polymer molecule with a positive charge localised on one of the surface carbon atoms, e an incident electron, e_C an electron in the conduction band, e_L an electron in a trap of energy level L lying below the conduction band of energy E, and k_4–k_8 are the rate constants of the corresponding reactions. Equation (8) implies the transfer of a conduction electron into the metallic substrate s under the influence of the potential gradient dv/dx. If we consider that stage (8) is rapid, i.e. that there will be no great accumulation of charge in the polymer, we have

$$[P^{+}] = [e_c] + [e_L] \simeq [e_L]. \tag{10}$$

On the assumption that concentrations are constant, and that stage (7) is much more rapid than stage (6), the rate of polymerisation can be expressed in the form

$$r = k_5 \sqrt{\frac{k_4 I}{k_7 \exp(-E_L/kT)}} [Bu_a]. \tag{11}$$

In the deduction of this equation and of Eqn. (A), reactions such as the formation of cross-links and unsaturated bonds, etc. have been disregarded, since they do not affect the rate of polymerisation.

It is seen from Eqns. (A) and (11) that in both cases the rate of polymerisation is proportional to the concentration of sorbed butadiene molecules and to the square root of the electron current: i.e. the type of dependence of r on $[Bu_a]$ and I provides no opportunity of assessing the mechanism of polymerisation. Hence it follows that additional data are necessary in order to elucidate the mechanism of polymerisation.

Experimental results are now available which indicate unambiguously that in several cases the radical mechanism of polymerisation may play a considerable part. Mayer [38] has shown that films can be obtained with electrons of energy below 6 eV, i.e. under conditions such that ions cannot be formed. This mechanism of polymerisation is supported also by the fact that the resulting films contain considerable concentrations of free radicals [28,29] (up to 10^{18} spins cm^{-3}). Christy [24] has given a theoretical expression for the rate of formation of films by a radical mechanism, which shows good agreement with his experimental data obtained with the vapour of silicone oil. Other authors [20,21,27] consider that in the cases which they have investigated films are formed also predominantly by a radical mechanism.

On the other hand, Haller and White [26], in a paper on the polymerisation of butadiene on a surface, give experimental data supporting an ionic mechanism. To determine the mechanism of polymerisation they used mixtures of butadiene with oxygen (4 : 1) and with hydrogen (1 : 4). If a

radical mechanism of polymerisation is assumed, the presence of oxygen should result either in complete suppression or to a slowing down of polymerisation; hydrogen should have a similar effect, and its presence should lead to an increase in the rate of migration of free radicals in the polymer and an increase in k_3 in Eqn. (3). It was found, however, that, within the limits of experimental error, the rates of polymerisation of pure butadiene and of its mixtures were the same when the partial pressures of butadiene in the mixtures were equal to its pressure in the experiments on the polymerisation of the pure monomer. This was regarded as indicating that butadiene polymerises by an ionic mechanism. This view is supported also by the fact that the life of positive ions in the polymer, determined[26,27] by means of a pulsed electron beam, is very long (around 1–3 min).

The preceding arguments have applied to the polymerisation of organic molecules on the surface of already formed polymer. However, formation of the first layer of polymer film directly on the pure metal surface has been found to involve far more rapid polymerisation than in the formation of subsequent layers. Hirsch[42], comparing his experimental results on the production of polymer films of monolayer thickness with those obtained by Ennos[20] on the formation of films several thousand Ångström units thick under roughly similar conditions, found that the rate of film growth was higher in the former case by factors of the order of 10^2. White[39] established that one incident electron causes the polymerisation of 30 butadiene molecules in the case of a pure metal surface, whereas on a previously formed film the polymerisation of one butadiene molecule requires 100 electrons. Such a difference in the rates of formation of the first layer of a film compared with that of subsequent layers is explained by the author in terms of the energy state of molecules adsorbed on the clean metal surface being such that only slight action by electrons is required for the chain reaction of polymerisation to begin. It must also be borne in mind that a high rate of formation of the initial layers of a film may be considerably affected also by secondary electrons dislodged from the substrate metal[36].

3. Structure and Properties of Films

Little work has been done on the structure of polymer films obtained on a surface by electron bombardment. This method probably does not allow films of ordered structure to be produced[38]. X-Ray examination has shown the films to be amorphous[19,33,43-45]. Infrared spectroscopy has been used in several cases to investigate the structure of the films. The infrared spectra[27] of films obtained, in an atmosphere of a silicone oil, on the surfaces of stainless steel and of an optically polished sodium chloride crystal contained in both cases a broad absorption band in the region of 1050 cm^{-1}, corresponding to stretching vibrations of the Si–O–Si group, together with absorption bands corresponding to vibrations of the $Si-CH_3$ bond, deformation vibrations of the Si–O bond, and oscillations of a hydrogen atom in CH_2 and CH_3 groups. The absorption spectrum of the film obtained on the metallic substrate also included a band in the region of 1750 cm^{-1}, indicating the presence of carbonyl groups in the film, and a broad band near 3400 cm^{-1}, corresponding to the hydroxy-group. The appearance of carbonyl and hydroxyl groups in the film is probably due to oxidising processes, as in the irradiation of ordinary polymer films with electrons[46,47]. The

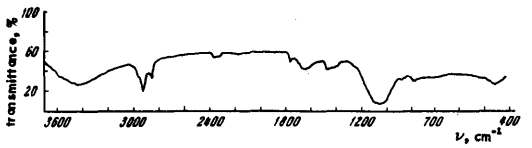
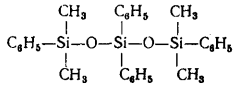


Fig. 3. Infrared spectrum of film obtained from silicone oil.

absorption band in the region of 1620 cm^{-1} for the film obtained on sodium chloride, and 1645 cm^{-1} for the film obtained on the metal, is especially interesting, for it indicates the presence of double bonds in the films. The infrared spectrum of the polymer film obtained on a stainless steel substrate is reproduced in Fig. 3.

The possible structure of films obtained from the silicone oil DS 704 is discussed by Holland and Laurenson[34]. The chemical formula of the oil (M = 484) is



The action of a discharge and of γ-rays on this compound in the gas phase gave large quantities of hydrogen and methane with little benzene. From this it is concluded that the phenyl group remains in the polymer molecule, the monomer units being linked by CH_2 and $CH_2.CH_2$ groups.

Several workers have examined the physical and chemical properties of the films[19,24,42-44]. Films obtained from organic compounds always contain carbon and hydrogen[19], sometimes also oxygen[11], and can be removed from the surface by heating in air to redness[10,19]. The films are insoluble in water, the usual organic solvents, and also strong acids and alkalis. They possess high thermal stability[10,43,44], especially those obtained from silicone oils[43]. The present method also enables especially thin films to be obtained, possessing good homogeneity[37], continuity[24,42], adhesion to the substrate surface[27,44], and superior dielectric properties[24,27].

Many studies have been made[10,24,27-29,34] of the electrical properties of films obtained in atmospheres of organic and silicone compounds. The film possess high values of the bulk resistivity R_v and the breakdown voltage[24,27]. Table 1 gives estimated values of R_v, the dielectric constant ϵ, the tangent of the loss angle $\tan\delta$, and the breakdown voltage v_{br} for films from silicone oil[27].

The electrical conductivity of the films varies between wide limits depending on the energy of the electrons, the temperature, and the material of the substrate. Poole[21] showed that films having a high resistance are obtained with electrons of energy below 300 eV, whereas films of low resistance are obtained above this value. Zinn[33] has investigated the influence of the substrate material on the insulating properties of the films: films obtained on

TABLE 1.

R_v, ohm cm	ϵ	$\tan\delta$	v_{br}, V cm^{-1}
$1\cdot10^{-14}$	3—4	<0.01	$>10^6$

aluminium and tin possess good insulation, those on lead have moderate insulation, and those on gold and silver possess no insulating properties. He suggests[33] that the good properties on aluminium and tin are due to thin oxide films at the metal–dielectric interface. Experiments on the influence of the substrate temperature on the electrical conductivity of the film show[34] that those obtained at 240°C have a resistance of 6.5×10^9 ohms cm^{-2}, while those produced at room temperature have a value of 10^{13} ohms cm^{-2}. Nevertheless, films obtained at +50°C and −196°C have identical insulating properties. The absence of variation in electrical conductivity with temperature over this range is attributed[34] to similar coefficients of adhesion of the silicone oil molecules at these temperatures.

Holland and Laurenson[34] have investigated the effect, on the dielectric properties of films obtained from silicone oil, of adding various gases (oxygen, nitrogen, hydrogen, carbon dioxide, and water vapour) during their preparation. It was found that addition of oxygen and water vapour to the silicone oil vapour resulted in films showing higher resistance in air than in a vacuum, whereas films obtained with additions of nitrogen, hydrogen, and carbon dioxide show a higher resistance in a vacuum. The latter result was explained by adsorption of water vapour on the surface of the film in air. The dielectric constant ϵ of the films was 2.3 and 4.0 with additions of carbon dioxide and hydrogen respectively.

A considerable growth of interest has recently occurred in the mechanism of the passage of current through thin insulating films, including polymer films; the main reason for this interest is the need to use them for controllable sources of current, such as cold-cathode emission devices and tunnel triodes. The principle on which such devices operate has been discussed[48]. Two main mechanisms by which electrons can be transmitted through thin insulating films—passage of current by the tunnel emission of electrons and by Schottky emission—have been considered in the literature, and can be distinguished by the dependence of current on voltage and temperature (Table 2). Transport of current by the tunnel effect is independent of temperature, and is observed in extremely thin films (~ 100 Å), where the mean free path of the electrons in the film is comparable with its thickness. Transport of current by the Schottky mechanism occurs with thicker films, and is strongly dependent on temperature.

Studies have been made of the mechanism by which current passes through thin polymer films and of their electrical properties[28,29,49]. Mann[28] has examined the electrical properties of films obtained in the vapour of the silicone oil DS 704. Measurements were made of the current in the M–P–M system, over the range of film thicknesses 500–2500 Å, as a function of voltage and temperature (the system comprised a polymer film P enclosed between two sputtered metal electrodes M). At voltages up to 5 V the current density varies exponentially with the electric field strength, and is independent of film thickness. When the voltage is increased above 5 V, the current decreases, to disappear completely at ~ 6 V. A typical curve showing the variation in current density I with voltage is shown in Fig. 4.

The electrical conductivity of the films is strongly dependent on temperature at high voltages, but at low voltages, in the region of the negative resistance effect, the conductivity is independent of temperature. Christy[29] has investigated the electrical properties of analogous films over the thickness range 50–150 Å, and found that at low voltages (< 1 V) the current increases linearly with voltage, whereas at higher voltages it obeys the law $\ln I \propto V^{1/2}$. An investigation[49] of the conductivity of a polymer film 100 Å thick showed that $\lg I \propto V^{1/2}$ for voltages from 0.04 to 1 V. The temperature dependence of current for this film is reproduced in Fig. 5. The departure of this curve from a straight line is explained by a mixed mechanism for the transmission of electrons: a current due to tunnel emission is superimposed on the current due to Schottky emission, and makes a particularly large contribution at low temperatures.

The effect of ageing the film in air on its electrical properties has been investigated[28,29]. The volt–ampere characteristics gradually move to the right as the films remain in the air, and at the same time the capacitance of

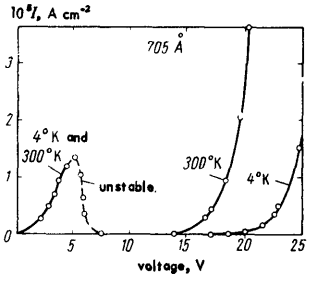


Fig. 4. Voltage dependence of current density in the M–P–M system.

TABLE 2. Dependence of current on voltage and temperature for two mechanisms of electron transfer.

Emission	Voltage dependence	Temperature dependence
Tunnel	$I \propto V$ for $I < \Phi$ $I \propto V^2 e^{-\text{const}/V}$ for high V	none
Schottky	$I = \alpha \exp(BV^{1/2})$	$I \propto T^2 e^{-\text{const}/T}$

Φ = work function between metal and polymer film; α and B are constants.

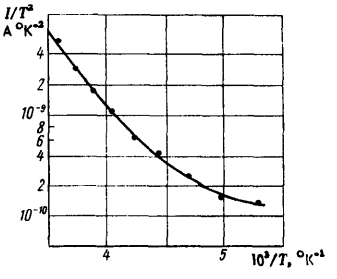


Fig. 5. Temperature dependence of current for a film obtained from the silicone oil DS 704.

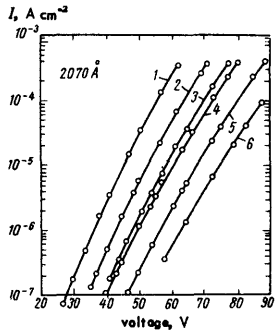


Fig.6. Dependence of current density on voltage for a film left in air over different periods.
1) 5 min; 2) 26 h; 3) 72 h; 4) 96 h; 5) 192 h; 6) 360 h.

the M–P–M system increases (Fig. 6). Placing the system in a desiccator resulted in a change in its electrical conductivity analogous to that occurring in the air, while the capacitance remained unchanged with time under these conditions. When, however, the system was placed in a vacuum or in an atmosphere of dry nitrogen, neither the conductivity nor the capacitance changed with time. It is concluded [28,29] that the change in conduction of the M–P–M system in air is associated with the adsorption and diffusion of oxygen molecules into the film through the electrodes, while the change in capacitance of the system is caused by the adsorption of water vapour. It has also been observed that the variation in the conductivity of films in air parallels the variation in the concentration of free radicals formed in the film during its preparation (the films contain high concentrations of free radicals, ~ 10^{18} spins cm^{-3}). This indicates that the mechanism of electrical conduction in the films is connected with free radicals, and that in this case the radicals are probably acting as electron-traps.

III. PRODUCTION OF POLYMER FILMS IN THE GLOW DISCHARGE

The chemical reactions leading to the formation of polymer films in the glow discharge are considerably more complicated and diverse than those occurring under the influence of a beam of electrons. This is due both to the high pressures and current densities (~ 1 mmHg and 0.1–1 mA cm^{-2}) and to the energy distribution of electrons in the discharge zone. A consequence of this distribution is that various electronic states in complicated organic molecules are already excited at the primary interaction step, so that a variety of dissociation fragments are formed. Furthermore, the breakdown of organic molecules may be caused by the action of free radicals and hydrogen atoms formed as a result of the primary reactions, since high pressures in the discharge zone favour the occurrence of secondary processes in the gas phase. It follows from this that the great diversity of chemical changes which organic molecules usually undergo under the influence of a glow discharge is not always due to the discharge itself, but is often a consequence of secondary processes caused by various neutral species. Hydrogen atoms can probably exert an especially large influence on chemical reactions in the discharge, since it has recently been established that they can possess high energies, close to the ionisation potential of the hydrogen atom, and the reaction cross-section for such excited particles far exceeds the usual gas-kinetic cross-section [50].

It follows from the above that film formation on a surface in a glow discharge may be caused not only by charged species, as occurs under the influence of electrons and ions, but also by active neutral species formed in the discharge zone, their concentration in the plasma far exceeding the concentration of charged species. It is also possible that ultraviolet radiation, produced by spontaneous loss of excitation by particles, may play some part in initiating the surface process.

As early as 1874 Thénard [51] and Wilde [52] noted that the action of an electric discharge on hydrocarbon vapours resulted in the formation of solid deposits on the walls of the apparatus. A later study (in the 1930s) of the chemical action of a glow discharge on methane showed [53] that, in a negative discharge at the temperature of liquid air, methane underwent dissociation followed by condensation. At room temperature dull yellow deposits were formed on the walls, which were unaffected by the usual solvents.

Austin and Black [54,55] studied the chemical behaviour of several cyclic hydrocarbons in a Tesla discharge. They found that a coating similar to shellac was formed on the walls of the reaction vessels, and solid reaction products condensed in a liquid nitrogen trap. With cyclohexane, benzene, toluene, and *p*-xylene the thin films resembling shellac were sometimes reddish brown or black in colour, and sometimes almost colourless. The freshly prepared films had good adhesion to the surface, but on standing they peeled off and cracked. The films did not dissolve in alcohol, acetone, ether, turpentine, benzene, toluene, xylene, or water, and were unaffected by the usual acids and alkalis. Elementary analysis of the films showed them to contain oxygen as well as carbon and hydrogen. From the results the formulae $(C_9H_7O_2)_x$, $(C_{21}H_{19}O_3)_x$, and $(C_{19}H_{19}O_3)_x$ were proposed for the solids present in the films formed from benzene, toluene, and xylene respectively.

Linder and Davis [56] investigated the behaviour of 57 different hydrocarbons in the discharge. In almost all cases they observed the formation of solid products on the cathode, the anode, and the walls of the discharge tube. These products were dark brown or black, mostly waxlike, but sometimes brittle. They evidently contained much carbon, although they did not burn completely on analysis.

Stewart [10], working with a discharge in a vacuum of around 10^{-5} mmHg, obtained insulating films which were insoluble in the usual solvents. He concluded that the films were of hydrocarbon origin, probably formed from residual gases and also from the vapour of the vacuum grease.

At the present time polymer films are obtained in a discharge usually under a vacuum bell jar at pressures of the order of 0.001–0.1 mmHg. [57-69] As an example let us consider the equipment for the production of thin polymer films patented by the [American] General Electric Co. [68] (Fig. 7). The pressure under the bell jar is ~ 0.02 mmHg, the electrodes are 16 mm apart, and the voltage between them is 1000 V. The optimum pressure range in the system is 0.01–0.1 mmHg. Polymer films less than 5 μm thick, possessing good dielectric characteristics, have

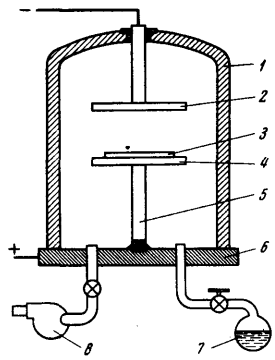


Fig. 7. Diagram of apparatus for the preparation of thin polymer films in a glow discharge:
1) vacuum bell jar; 2), 4) electrodes; 3) plate on which a film is sputtered; 5) electrically conducting support; 6) tile; 7) vessel containing initial monomer; 8) pump.

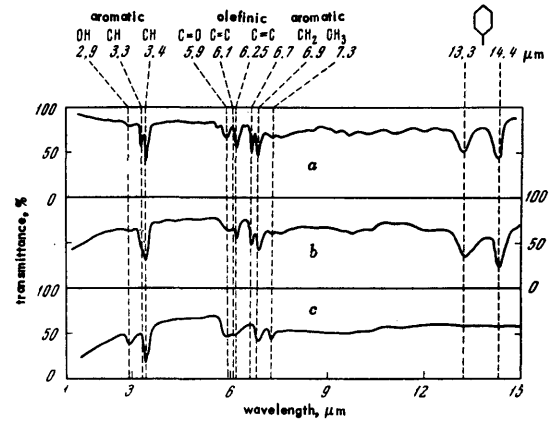


Fig. 8. Infrared spectra of polymer films obtained from benzene and methane:
a) polystyrene foil irradiated with electrons; *b*) polymer film obtained from benzene; *c*) polymer film obtained from methane.

been obtained by this technique. The substrates on which the films are deposited have usually been of synthetic rubber metallised with aluminium, but films can be deposited on other materials—glass to which a surface layer of metal has been applied, metallic and siliceous plates, etc.

Coleman[61] uses as substrates moving tapes, which are gradually removed from the discharge zone, to obtain films of constant thickness undamaged by the heat evolved in the process.

König and Helwig[70] and Brockes and König[71] studied polymer films obtained from benzene vapour. In the former case[70] the discharge current was 7–9 mA and the voltage ~ 1000 V. The elementary composition of the film was determined ($C_{1.00}H_{0.83}$), its mass (by weighing on a quartz balance), its thickness with a Zener interferometer, and its density. These films proved to be less dense than carbon or graphite. The electrical conductivity of the films was ~ 10^{-9} ohm^{-1} cm^{-1}. The properties of the films were considerably changed by vacuum heat-treatment above 100°C. The optical transmission of the films was substantially diminished, and at 400°C they became first brown and then black. Heating the films produced an especially marked change in their electrical conductivity, which had increased by factors of 10^{10} after heating to 600°C.

Infrared spectroscopy was used[71] to establish the structure of the films. The infrared spectra of films obtained from benzene contained absorption bands characteristic of aromatic groups, whereas these bands were absent from the spectra of films obtained from methane (Fig. 8). It is interesting that the infrared spectra of a polymer film obtained from benzene and of a polystyrene film which had been irradiated with electrons had much in common with respect to both the character and the intensity of the bands. On storage in air the films underwent oxidation, and the infrared spectra contained bands corresponding to C=O and O–H bonds. Similar bands were observed also after irradiation of the film with electrons. Infrared spectroscopy was used also to investigate the oxidation of films from benzene as a function of their storage time in air (Fig. 9).

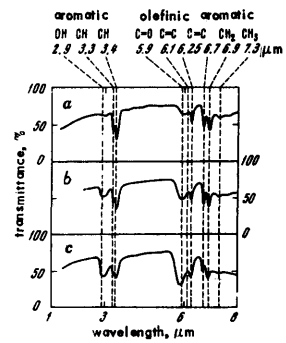


Fig. 9. Variation in infrared spectrum of polymer films obtained from benzene with time of storage in air:
a) 2 h; *b*) 5 days; *c*) 1 month.

If the films were heated in a vacuum immediately after preparation, they underwent no subsequent oxidation in air.

The influence of the conditions and parameters of the discharge on the properties of the resulting films was also investigated. An appreciable decrease in the hydrogen content of the films was observed, together with a diminished rate of film growth, when the discharge voltage was increased to 3000 V. Increase in the voltage also produced an increase in the quantity of degradation products of low molecular weight and the number of conjugated double bonds formed.

Pagnia[62,72] showed that the properties of films obtained in benzene vapour in a glow discharge depend to a considerable extent on the conditions of the discharge. With the same ignition voltage the films differ in electrical conductivity depending on whether the substrate is cooler or heated: it has the values 0.1 and 100 ohm^{-1} cm^{-1} respectively. Pagnia put forward the hypothesis that, with high ignition voltages and "hot" substrates, the films consist of

carbon alone, which may explain their relatively high conductance and great stability. This hypothesis was confirmed by the infrared spectra: the carbon content of films obtained with a "hot" substrate was very high, while the hydrogen content was insignificant. Nevertheless, the vacuum annealing of films obtained at low ignition voltages leads to a considerable loss in weight. The dependence of the resistivity on the ignition voltage, taking into account the temperature of the substrate, is illustrated in Fig. 10. Pagnia showed also that the resistance of the films remains constant on storage in a vacuum, but increases on storage in air, reaching a constant value only after several days (Fig. 11). Furthermore, all types of films obtained showed an increase in conductance with temperature.

Vastola and Wightman[73] also studied the behaviour of several hydrocarbons—ethane, methane, and ethylene (Group A) and acetylene, benzene, and naphthalene (Group B)—in a high-frequency discharge. The main product with both groups of hydrocarbons was a film a few Ångström units thick having a definite H/C ratio, and almost all the films absorbed a further quantity of hydrogen from the discharge, the ratio reaching a limiting value of 1.6. The films were insoluble in organic solvents. They were shown to be amorphous by X-ray and electron diffraction. The infrared spectra showed films of Group B to possess greater unsaturation than those of Group A, and the latter contained no aromatic groups. A high concentration of free radicals was found in films of Group B. According to the authors these results were consistent only with a mechanism of film formation which was independent of the type of bond in the initial hydrocarbon.

The electrical properties of films obtained in the glow discharge from 40 different substances have been investigated by Bradley and Hammes[57,74] and by Bradley[75]. The films were prepared at a pressure of ~ 1 mmHg, a current density of 1–3 mA cm^{-2}, and a voltage of 300–400 V, the thickness of the films being controlled by the discharge current and the time. These authors assume that the

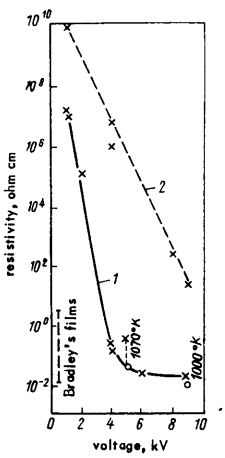


Fig. 10. Dependence of resistivity of film on ignition voltage of discharge with the temperature of the substrate taken into account:
1) substrate heated at 675° ± 15°K;
2) substrate cooled.

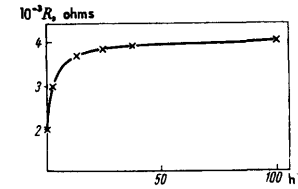


Fig. 11. Variation in resistance of film with duration of exposure to the air.

mechanism of conduction in the films studied in the same to a first approximation, although differences are observed in the structure, appearance, and stability of the films. The absorption of oxygen has no fundamental effect on the conductance (which is approximately doubled on the absorption of ~ 10 wt. % of oxygen). It was suggested that the magnitude and temperature dependence of the conductance are explained by the predominance of C–C bonds in the film structure. The same workers[74] investigated the photoconduction of films obtained in the glow discharge and containing nitrogen, sulphur, selenium, and several metals. They showed that the photoconductance varies by several orders of magnitude depending on the composition of the films, and a considerable increase in the photocurrent is observed with rise in temperature from −77°C to 185°C. The principal factor associated with photoconduction is probably the concentration of unsaturated groups in the films.

Bradley[75] has investigated the dark conductance and the photoconductance of polymer films obtained in a discharge, as functions of the temperature and the voltage during measurement. With most of the specimens examined the current was proportional to the voltage raised to a power exceeding unity: $I \propto V^{\Delta}$ ($\Delta > 1$). With many specimens the exponent Δ remains constant over a wide range of temperatures, although some highly conducting films show a sharp increase on heating above 180°C, after which Δ remains unchanged on cooling to room temperature. Films obtained from several sulphur, selenium, and nitrogen compounds gave values of the exponent Δ = 1–1.3, with the exception of films prepared from malononitrile. Such films and also those obtained from ferrocene exhibit a considerable increase in Δ on heating to 180°C. The activation energy of conduction was also determined, and for most of the films proved to be 0.4 ± 0.1 eV. It drops appreciably below 0°C, and may reach 0.1–0.2 eV. The author remarks that no theory is yet available to explain the temperature variation of Δ and of the activation energy.

Several papers have discussed a suggested mechanism for film formation in the glow discharge[57,60,76–78]. Goodman[60] assumes that ionised species form a polymeric substance on the electrode surfaces. Since the resulting polymer is again bombarded by ions, the same consequences—degradation and cross-linking—can be expected as with high-energy irradiation. Bradley and Hammes[57] proposed a mechanism consisting in the formation of ionic and radical-ion fragments by the intense electron bombardment, with recombination of these fragments on the electrodes. Haefer[76,77] assumes that molecules are ionised in the gas space of the glow discharge, forming intermediate products—free radical-ions—which exhibit a great tendency to recombine, and on striking the electrode surfaces form solid polymers.

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Thus investigators have reached essentially the same view of the possible mechanism of film formation in a discharge. On the basis of this type of mechanism, Haefer has calculated $p_1 = dp/dt$, the number of molecules entering a layer of the film of area 1 cm² in 1 s. If N molecules are adsorbed on 1 cm² of the electrode, we have

$$p_1 = \sigma \cdot j \cdot N \qquad (1)$$

where j is the number of charged particles on 1 cm² after 1 s, and σ the ionisation cross-section of a sorbed molecule on electron or ion impact. Let us consider two extreme cases, in which (1) the vapour pressure ensures a complete monolayer, or (2) the monolayer is incomplete.

In the former case the partial pressure of the starting material is quite high. The number of molecules F of the gas phase incident on unit surface in 1 s is then large compared with the rate of film formation p_1. During the first few moments the surface becomes covered with a monolayer: $N = 1/a$, where a is the surface necessary for the adsorption of one molecule. In this case the rate of growth of the polymer film is

$$p_1 = \frac{\sigma}{a} \cdot j. \qquad (2)$$

Experimental support for this conclusion has been given by Haefer and Mohamed [77].

If the number of adsorbed molecules is even less than a monolayer, i.e. if $N < 1/a$, we have

$$\frac{dN}{dt} = F - \frac{N}{\tau} - p_1 = F - \frac{N}{t} - \sigma j N = 0 \qquad (3)$$

where τ is the life of an adsorbed molecule. From Eqn. (3) we find that

$$N = \frac{F}{\sigma j + \frac{1}{\tau}} \qquad (4)$$

and from Eqns. (1) and (4) we obtain

$$p_1 = \frac{\sigma j F}{\sigma j + \frac{1}{\tau}} = \frac{F}{1 + \frac{1}{\sigma \tau j}}. \qquad (5)$$

Two cases can be distinguished:

1) $\sigma\tau j \ll 1$, then $p_1 = \sigma\tau j \cdot F$ (5a)

i.e. at low current densities and with small interaction cross-sections the rate of growth of the polymer film is proportional to the current density and the vapour pressure.

2) $\sigma\tau j \gg 1$ then $p_1 = F$ (5b)

i.e. at high current densities and with a large interaction cross-section the rate of growth reaches a limiting value: every molecule striking the electrode enters the polymer. This theory is supported by measurements made with oil molecules under conditions of electron impact [24,30,32,45].

A somewhat different mechanism for the formation of coating films in the glow discharge is suggested by Haisen [78], who assumes that the layers are formed from fragments produced, not in the gas space, but directly on the surface of the object. Particles incident on the surface, and carrying excess energy, split up the adsorbed hydrocarbon molecules, and the resulting fragments recombine to form a solid deposit. However, the author does not give sufficiently convincing experimental evidence in support of this view.

Film formation in a discharge has been studied not only with hydrocarbons which are incapable of ordinary chain polymerisation but also with typical monomers. Rubanovskii [79] studied the kinetics of the polymerisation of butadiene in the glow discharge, and observed the deposition of a solid polymer on the walls of the discharge tube and on the electrodes. He showed also that polymerisation is excited not only by the impact of electrons but also by that of hydrogen atoms. The process of polymerisation exhibits a clearly marked induction period.

The discharge polymerisation of one of the most widely investigated monomers, styrene, has been studied by Stuart [58], who obtained polystyrene films insoluble both in water and inorganic solvents. Electron spin resonance measurements, made in a vacuum at room temperature, showed the presence of free radicals, which most probably underwent oxidation to peroxide in air.

The production of solid polymers from several typical monomers in a discharge has been referred to in other papers [56,57,60,73]. However, it is only recently that the behaviour of typical monomers and polymers in a discharge has begun to be studied more thoroughly.

DaSilva and Miller [63] studied the rates of formation of polymer films from butadiene and vinyl chloride. They showed that, after the discharge has operated for 3 min, butadiene gives a film 400 Å thick at a gas pressure of 100 mmHg, whereas with vinyl chloride the rate of deposition is 30 Å s^{-1} (if the discharge current is 70–90 mA, and the voltage 100–150 V). The electrical properties of polybutadiene films obtained in a discharge (pressure 0.3–0.55 mmHg, voltage 350–400 V, and current 6–8 mA) have been studied by Bashara and Doty [66], who assume the films to consist of poly-1,4-butadiene and to be extremely strongly cross-linked. They found the resistivity of such films to be $\sim 10^{11}$ ohm cm.

Holland [80] studied the behaviour of several polymeric materials—polyethylene, polystyrene, epichlorohydrin resin, cross-linked melamine—in a discharge of voltage 5 kV and current density 0.13 mA cm^{-2} with cooled specimens in an atmosphere of air or argon. He showed that the cathodic samples became brown and non-transparent 50 min after the start of an experiment. Under the action of electrons the specimens underwent surface pitting, and ions sometimes caused "erosion" of the surface.

The action of a discharge on the surface of polymer films led to the idea that a polymer might be activated in a discharge with the aim of subsequent grafting. Korshak et al. [65] used the activation of polytetrafluoroethylene in a discharge in order to initiate on its surface the graft polymerisation of vinyl monomers with the object of improving the adhesive properties of the material. Special apparatus was used for a discharge of frequency 50 c/s and voltage 22–30 kV. The film obtained from tetrafluoroethylene was placed in the discharge zone for 10–30 min, then immersed in a vessel containing the vinyl monomer, and copolymerised at 85–90°C. Such grafting considerably improved the adhesion of the polytetrafluoroethylene to steel and other materials.

The production of films in a glow discharge is of very considerable value for the recently started wide application of silica and organosilicon films as surface passivators and diffusion coatings in microelectronics.

Leslie et al. [81] studied the low-temperature deposition of silica films, for which purpose an organic silicone (an

alkoxysilane) was decomposed in an argon plasma. Breakdown of the silicone molecules on collision with ionised and excited argon atoms took place on the electrode surface, where a stable Si–O–Si lattice was formed. The rate of deposition was studied as function of the flux of ions, the power of the discharge, the temperature, and the geometry of the substrate. The resulting silica films were studied by various methods: electron diffraction confirmed their amorphous structure, and the infrared spectra showed the absence of C–H bonds. Ing and Davern[82] also prepared silica films for coating semiconductors. Deposition was conducted in tetraethylsilane vapour in a glow discharge. The resulting film was homogeneous, and possessed good adhesion to a gallium arsenide surface. Such a film was 1800–2000 Å thick. These workers have subsequently investigated[83] thin silica films obtained from tetraethoxysilane in a discharge. These films can be successfully used as dielectrics in thin-film capacitors.

IV. PRODUCTION OF POLYMER FILMS ON EXPOSURE TO ULTRAVIOLET RADIATION

The chemical processes occurring under the influence of ultraviolet radiation, and leading to the formation of polymeric deposits on solid surfaces, resemble in many respects the analogous processes occurring on electron bombardment. It must be noted, however, that photochemical investigations in this field, which were begun in 1910 and continue at the present time, have mainly been purely descriptive and qualitative in character.

In 1910 Berthelot and Gaudechon[84] observed the formation of polymeric solid deposits on the walls of the reaction vessel when acetylene was exposed to ultraviolet radiation. The yellow film obtained was similar in appearance to that formed by the action of a discharge on acetylene. Even certain kinetic aspects of the formation of films of this kind were noted: the rate of deposition of films slowed down in the course of growth owing to absorption by them of ultraviolet radiation, and the rate of conversion of acetylene into solid polymer was approximately doubled in the presence of an inert gas.

Lind and Livingston[85], while studying the photochemical polymerisation of acetylene, observed the deposition of a solid polymer on the window through which the ultraviolet irradiation occurred, this resulting in diminished transparency of the window and a fall in the rate of polymerisation.

Bates and Taylor[86] and also Reinicke[87], while investigating the photoexcitation of ethylene and acetylene, also noted the formation of a solid polymer, insoluble in organic solvents.

Olson and Meyers[88] obtained polymeric solid deposits on the walls of a reaction chamber in which ethylene had been subjected to ultraviolet irradiation. The deposits were detected from the interference colours and also from the effect on the rates of subsequent reactions. Kemula and Mrazek[89] studied the mechanism of the photopolymerisation of acetylene, and found among the many polymerisation products a yellowish solid deposited on the walls of the reaction vessel. This substance absorbed the active part of the radiation very strongly, and diminished the reaction velocity. Livingston and Schiflett[90], who studied the photopolymerisation of methylene at high temperatures, detected two non-volatile solid products, one of them resembling cuprene, while the other formed a film recalling a dark yellow dried lacquer film. On heating the film charred, but it burned in air only with difficulty, forming a compact coating which adhered well to the surface. This film was partly soluble in ether, which was coloured a dark yellow. Melville[91] showed that the maximum permissible gas pressure in the vessel during the photochemical polymerisation of ethylene and acetylene was 10 mmHg, since at higher pressures deposits of a solid polymer were formed on the walls of the reaction vessel. The formation of solid films during the photopolymerisation of acetylene was noted also by Le Roy and Steacie[92]. The films could be removed by burning them off after an experiment. Numerous studies of the photopolymerisation of acetylene and ethylene were collated in Steacie's book[93], but in nearly all of these the authors had merely noted the formation of solid polymer films and described their properties sketchily. Nevertheless, even in the more recent work of the 1950s and 1960s the preparation of polymer films by ultraviolet irradiation has not been a subject of independent study. Zelikoff and Aschenbrand[94], while investigating the photochemistry of the vacuum ultraviolet, noted the formation of a solid polymer on the walls of an acetylene reaction vessel, and the consequent diminution in its transparency. The coating which had absorbed the ultraviolet radiation was formed in about 3 min. The resulting film was decomposed by nitric acid. DeCarlo et al.[95] also noted the formation of solid polymers by the ultraviolet irradiation of acetylene.

Although the polymer films formed on a solid surface by the action of ultraviolet radiation have not become a subject of independent study, several authors have nevertheless suggested possible mechanisms for their formation. Whereas in the early papers of the 1930s preference was given to a mechanism involving excited molecules, Steacie[93] was inclined to adhere to a free-radical mechanism.

All workers who have observed films of this type on ultraviolet irradiation have noted their good adhesion to the surface on which they had been deposited, their high thermal stability, and their resistance to many solvents.

V. APPLICATION OF FILMS

It has been shown above that polymer films obtained by the action of electrons and in a glow discharge possess good dielectric properties. They possess also great strength, good surface adhesion, high thermal stability, and a lack of pores. The method permits very thin films to be obtained. All this suggests that the use of such films as dielectric layers in capacitors is very promising. Several patents[61,68,69] have proposed the use for this purpose of polymer films obtained in a discharge. Use of polymer films of this type permits a considerable increase in the capacitance per unit volume of the condenser and a substantial decrease in the size of the latter. Other methods of obtaining thin (around 1–2 μm) dielectric films have been tried[68], but none has given good results, mainly because the capacitors rapidly became defective owing to breakdown of the dielectric layer. The poor quality of the films—presence of pores, and also various types of impurities—proved to be the cause of the breakdowns. These defects are absent in polymer films obtained in a discharge, since the dielectric layer is then obtained directly on the surface on which it is to be used. A great advantage of capacitors made with films obtained in this way is also their excellent temperature stability, for they

can work at temperatures from −55° to +200°C.[68] A British patent[68] proposes the use as dielectric layers of polymer films 0.01–1 μm thick obtained from unsaturated aromatic or aliphatic compounds in a glow discharge. To obtain organic films of specified thickness in this case, a synthetic, e.g. polyethylene, film, which has first been coated with a thin layer of aluminium, is drawn through the discharge zone at a constant speed, which determines the thickness of the newly formed film if the discharge parameters are kept constant. A second layer of metal is applied to the resulting film by sputtering. The conditions of the discharge comprised an optimum pressure of the organic substance in the discharge zone of 10–100 μm, and an ignition voltage of the discharge of 300–2000 V. Either direct or alternating current can be used to obtain the dielectric films. A necessary condition for the production of homogeneous films is the presence of a steady visible discharge in the region between the electrodes.

Various methods of obtaining dielectric films in capacitors, including use of a glow discharge, have been surveyed[96], and use of polytetrafluoroethylene films obtained in a glow discharge as dielectric layers is claimed to yield excellent thin-film capacitors[97]. Coleman[61] and the Radiation Research Corporation[67] have suggested designs for special apparatus for the production of homogeneous and especially thin polymer films in a discharge, which can be used for the manufacture of capacitors. Hopf[98] states that polymerisation in a discharge is one of the cheapest methods for obtaining capacitor layers and protective coatings.

It has been suggested[99,100] that polymer films, formed on a surface under the influence of a glow discharge, might be used as anticorrosive protective coatings. Production of the coatings involves preparing the film itself, hardening it, and drying it at a definite temperature. Styrene and other monomers of the vinyl series have been used as film-forming material. The metal to be coated with a protective film was used as electrodes in the discharge chamber at a voltage of 300–1000 V. Coatings 0.1–0.5 mm thick were obtained. A typical consumption of electrical energy is 1 kW h for the production of 50 g of film. Sandford[99] has compared the properties of metallic and non-metallic protective coatings on metals, including polymer films applied in a discharge, and has reached the conclusion that the polymer coatings fully replace the former and, moreover, are cheaper.

Buck and Shoulders[101] proposed the use of films, obtained from organic substances by the action of electrons, as dielectrics in microelectronic circuits. These films can probably be utilised both for the manufacture of microcapacitors and to protect the final circuit from the atmosphere. An analogous application of polymer films has been mentioned elsewhere[37]. The semiconductor films obtained by Christy[25] point to the possibility of producing film diodes, and study of the mechanism by which current flows through very thin polymer films[48,49] shows that it is possible in principle to make thin-film tunnel triodes.

The method of applying polymer coatings in a glow discharge has been used for a long time to obtain replicas from small objects in electron-microscopic investigations[64,70]. The method consists essentially in coating the surface of the object which is to be examined in the electron microscope with an organic film, using benzene vapour in a glow discharge. The object is then heated in a high vacuum to 400°C, when the organic film is converted into a carbon film. After this the material of the object itself is decomposed chemically, so that only the carbon sheath remains, which is penetrated strongly by the electron beam. This method enables the finest surface details of particles to be observed.

The production of polymer films by the action of electrons has been proposed[102,103] for the manufacture of diffraction gratings, and also[45] for the production of optical interference filters.

Hirsch[42] suggested using this phenomenon, of the deposition of a polymer film on a surface bombarded with electrons, for focussing beams in the design of electronic apparatus. At points bombarded by electrons images are obtained, invisible to the eyes, caused by the formation of very thin polymer films. This latent image can be made visible by developing it by electrodeposition in copper sulphate solution. This method of obtaining the focal characteristics of an electron beam makes it possible to obtain images even with electrons of very low energies (up to 5 eV).

Bradley[75] has shown that polymer films obtained in a discharge possess great photosensitivity. This had again been pointed out by Mayer[38], who had investigated films obtained under the influence of an electron beam, and found them to possess photosensitivity in the visible and near infrared region. These properties of the films can be utilised in photosensitive high-temperature detectors[74].

Woodman[43] has proposed the use of silica films as diffusion masks for protecting a germanium surface from the diffusion of indium and antimony into it, which may be of value in the production of germanium diodes and triodes. In this work the silica films were obtained by electron bombardment of a germanium surface on which a thin film of phenylsilanol had first been condensed from the vapour. The resulting polymer film was oxidised in air at 500°C until pure silicon dioxide was obtained. It was found that a silica film on the germanium surface was completely impermeable to antimony, but permeable to indium.

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In the present paper we have summarised published information on the formation of polymeric organic films on solid surfaces by the action of active particles. A survey of the information given here shows that researches in this field have been quite widely developed in several countries, and even have already found practical application in the production of protective coatings and thin-film condensers, which possess high specific capacitance. The method discussed in this paper appears to us to open up several novel and interesting technical possibilities, and merits the attention of research workers in our own country.

1. G. Moore, J. Appl. Phys., 32, 1241 (1961).
2. I. Filosofo and A. Rostagni, Phys. Rev., 75, 1269 (1949).
3. L. James, I. Leck, and G. Carter, Brit. J. Appl. Phys., 15, 681 (1964).
4. P. Marmet and J. Morrison, J. Chem. Phys., 36, 123 (1962).
5. Y. Sasaki, J. Chem. Phys., 27, 281 (1957).
6. I. Ohta, J. Appl. Phys. (Japan), 29, 826 (1960).
7. B. L. Tsetlin, A. V. Vlasov, P. Ya. Glazunov, N. V. Mikhailov, Yu. L. Morozov, L. I. Plotnikova, S. R. Rafikov, L. G. Tokareva, D. Ya. Tsvankin, and M. V. Shlabygin, Collected Papers, "Radiatsionnaya Khimiya Polimerov" (Radiation

Chemistry of Polymers), Nauka, Moscow, 1966, p.131.
8. B.L.Tsetlin, S.R.Rafikov, L.I.Plotnikova, and P.Ya.Glazunov, "Trudy II Vsesoyuznogo Soveshchaniya po Radiatsionnoi Khimii" (Proceedings of the Second All-Union Conference on Radiation Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1962, p.497.
9. B.L.Tsetlin, "Industrial Uses of Large Radiation Sources", International Atomic Energy Agency, Vienna, 1963, Vol.1.
10. R.L.Stewart, Phys.Rev., [2], 45, 488 (1934).
11. J.Hillier and R.F.Baker, J.Appl.Phys., 15, 663 (1944).
12. J.Hillier and R.F.Baker, J.Appl.Phys., 16, 266 (1945).
13. N.Davidson and J.Hillier, J.Appl.Phys., 18, 499 (1947).
14. F.Grasenick and R.Haefer, Phys.Verh., 4, 102 (1954).
15. H.König and A.Winkler, Naturwiss., 35, 136 (1948).
16. H.König, Naturwiss., 35, 261 (1948).
17. V.E.Cosslett, J.Appl.Phys., 18, 844 (1947).
18. J.Watson, J.Appl.Phys., 18, 153 (1947).
19. J.Hillier, J.Appl.Phys., 19, 226 (1948).
20. A.Ennos, Brit.J.Appl.Phys., 4, 101 (1953).
21. K.Poole, Proc.Phys.Soc., B66, 542 (1953).
22. R.Haefer, Acta Phys.Austriaca, 9, 1 (1954).
23. A.Ellis, I.Burton, and C.Sennet, Nature, 160, 565 (1947).
24. R.Christy, J.Appl.Phys., 31, 1680 (1960).
25. R.Christy, J.Appl.Phys., 33, 1884 (1962).
26. I.Haller and P.White, J.Phys.Chem., 67, 1784 (1963).
27. A.K.Tsapuk and V.M.Kolotyrkin, Vysokomol.Soed., 10, 1802 (1965).
28. H.Mann, J.Appl.Phys., 35, 2173 (1964).
29. R.Christy, J.Appl.Phys., 35, 2179 (1964).
30. A.Ennos, Brit.J.Appl.Phys., 5, 27 (1954).
31. S.Leisegang, "Proceedings of the Third International Conference on Electron Microscopy, London, 1954", Royal Microscopical Society, London, 1956, p.184.
32. S.Leisegang and O.Schott, "Proceedings of the Stockholm Conference on Electron Microscopy, 1956", Academic Press, New York, 1957.
33. W.Zinn, Z.angew.Phys., 16, 115 (1963).
34. L.Holland and L.Laurenson, Vacuum, 14, 325 (1964).
35. G.Möllenstedt and W.Hubig, Optik, 11, 528 (1954).
36. H.Mann, Eletrochem.Technol., 1, 287 (1963).
37. Brit.Comm.Electron., 9, 851 (1962).
38. L.Mayer, J.Appl.Phys., 34, 2088 (1963).
39. P.White, J.Phys.Chem., 67, 2493 (1963).
40. A.Baker and W.Morris, Rev.Sci.Instr., 32, 458 (1961).
41. Industrial Electronics, 1, 118 (1962).
42. E.H.Hirsch, Brit.J.Appl.Phys., 11, 547 (1960).
43. T.Woodman, Brit.J.Appl.Phys., 16, 359 (1965).
44. J.McLennan, M.Perrin, and H.Ireton, Proc.Roy.Soc., A125, 246 (1929).
45. R.Speidel, Z.Physik, 154, 238 (1959).
46. A.Brockes, Z.Physik, 149, 353 (1957).
47. A.Brockes and R.Kaiser, Naturwiss., 43, 53 (1956).
48. E.Roderick, Brit.J.Appl.Phys., 15, 613 (1964).
49. P.R.Emtage and W.Tantraporn, Phys.Rev.Letters, 8, 267 (1962).
50. S.E.Kupriyanov, Zhur.Eksper.Teor.Fiz., 48, 467 (1967).
51. A.Thénard, Compt.rend., 78, 219 (1874).
52. M.P.Wilde, Ber., 7, 352 (1874).
53. A.Brewer and R.Kueck, J.Phys.Chem., 35, 1293 (1931).
54. J.Austin and J.Black, J.Amer.Chem.Soc., 52, 4552 (1930).
55. J.Austin and J.Black, Phys.Rev., 35, 452 (1930).
56. E.Linder and A.Davis, J.Phys.Chem., 35, 3649 (1931).
57. A.Bradley and J.P.Hammes, J.Electrochem.Soc., 110, 15 (1963).
58. M.Stuart, Nature, 199, 59 (1963).
59. L.Holland, Brit.J.Appl.Phys., 9, 410 (1958).
60. J.Goodman, J.Polymer Sci., 44, 551 (1960).
61. J.Coleman, U.S.P. 3 068 510 (18th December 1962).
62. H.Pagnia, Phys.Status Solidi, 1, 499 (1961).
63. E.M.DaSilva and R.E.Miller, Electrochem.Technol., 2, 147 (1964).
64. G.Mollenstedt and R.Speidel, Z.angew.Phys., 13, 231 (1961).
65. V.V.Korshak, K.K.Mozgova, and T.M.Babchintser, Dokl.Akad.Nauk SSSR, 151, 1332 (1963).
66. N.M.Bashara and C.T.Doty, J.Appl.Phys., 35, 3498 (1964).
67. Electrical Design News, 5, No.10, 6 (1960).
68. General Electric Co. [U.S.A.]; B.P. 905 713 (1959).
69. J.Goodman, U.S.P. 2 932 591 (1960).
70. H.König and G.Helwig, Z.Physik, 129, 491 (1951).
71. A.Brockes and H.König, Z.Physik, 152, 75 (1958).
72. H.Pagnia, Phys.Status Solidi, 1, 90 (1961).
73. F.J.Vastola and J.P.Wightman, J.Appl.Chem., 14, 69 (1964).
74. A.Bradley, Trans.Faraday Soc., 61, 773 (1965).
75. A.Bradley, Insulation (Libertyville), 10, No.4, 31 (1964).
76. R.Haefer, Rep.der Balzers AG. für Hochvakuumtechnik und dünne Schichten, Vienna, 1960.
77. R.Haefer and A.A.Mohamed, Acta Phys.Austriaca, 11, 193 (1958).
78. A.Haisen, Ann.Physik, [7], 2, 23 (1958).
79. L.Rubanovskii, Zhur.Fiz.Khim., 4, 431 (1933).
80. L.Holland, Nature, 181, 1727 (1958).
81. L.Leslie, S.W.Ing, and K,Laendle, J.Electrochem.Soc., 110, 465 (1963).
82. S.W.Ing and W.Davern, J.Electrochem.Soc., 111, 120 (1964).
83. S.W.Ing and W.Davern, J.Electrochem.Soc., 112, 284 (1965).
84. D.Berthelot and H.Gaudechon, Compt.rend., 150, 1169 (1910).
85. S.Lind and R.Livingston, J.Amer.Chem.Soc., 54, 94 (1932).
86. J.Bates and H.Taylor, J.Amer.Chem.Soc., 49, 2438 (1927).
87. H.Reinicke, Z.angew.Chem., 41, 1144 (1928).
88. A.R.Olson and C.H.Meyers, J.Amer.Chem.Soc., 48, 389 (1926).
89. W.Kemula and S.Mrazek, Z.phys.Chem., B23, 358 (1933).
90. R.Livingston and C.H.Schiflett, J.Phys.Chem., 38, 377 (1934).
91. H.W.Melville, Trans.Faraday Soc., 32, 258 (1936).
92. D.J.Le Roy and E.W.R.Steacie, J.Chem.Phys., 12, 117 (1944).
93. E.W.R.Steacie, "Atomic and Free Radical Reactions", Reinhold Publishing Corp., New York, 1954, Vols.1 and 2.
94. M.Zelikoff and L.M.Aschenbrand, J.Chem.Phys., 24, 1034 (1956).
95. L.J.Stief, V.J.DeCarlo, and R.J.Mataloni, J.Chem.Phys., 42, 3113 (1965).
96. D.A.McLeon, Proc.Inst.Elec.Engrs., B109, Suppl.No.22, 457 (1962).
97. Proc.Electro.Components Conf. 1960, Washington.
98. P.Hopf, Rubber Plastics Age, 46, 391 (1965).
99. J.E.Sandford, Iron Age, Metalworking International, 3, No.10, 13 (1964).
100. Iron Age, Metalworking International, 4, No.1, 22 (1965).
101. D.A.Buck and K.Shoulders, "Proceedings of the Eastern Joint Computer Conference, 1958", American Institute of Electrical Engineers, Philadelphia, 1959, p.55.
102. G.Möllenstedt and R.Speidel, Z.angew.Phys., 16, 347 (1963).
103. G.Möllenstedt and C.Jönsson, Z.Physik, 155, 472 (1959).

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