

01 Sep 1983

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### Recommended Citation

M. Gazicki and H. Yasuda, "Electrical Properties Of Plasma-polymerized Thin Organic Films," *Plasma Chemistry and Plasma Processing*, vol. 3, no. 3, pp. 279 - 327, Springer, Sep 1983.

The definitive version is available at <https://doi.org/10.1007/BF00564629>

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## Electrical Properties of Plasma-Polymerized Thin Organic Films

Maciej Gazicki<sup>1</sup> and H. Yasuda<sup>1</sup>

Received January 25, 1983; revised May 31, 1983

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*The electrical properties of plasma-polymerized films are summarized and compared to those of conventional polymers. Particular attention is devoted to the dielectric relaxation, dielectric breakdown, electric conductivity and photoconductivity, and their control via control of the plasma parameters.*

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**KEY WORDS:** Plasma polymerization; dielectric properties of polymers; electric conductivity; photoconductivity.

### 1. INTRODUCTION

It can be stated without doubt that interest in the plasma polymerization process originated from the desire to find technological applications for thin dielectric films obtained from this process. Although thin solid deposits have been observed by researchers investigating organic vapor plasmas, they were usually considered to be undesirable by-products and were never characterized. In 1956, however, the Radiation Research Corporation (RRC) team working on radioisotope energy conversion devices (nuclear batteries) attempted to apply a glow-discharge-polymerized thin film as a dielectric part of their battery. They deposited 1  $\mu\text{m}$  glow-discharge-polymerized styrene on tritiated titanium foil, and it turned out to be a satisfactory dielectric material separating the electrodes of their device.

The nuclear battery project was sponsored by the U.S. Army, and the results of the studies were not published. However, since the device was never accepted into production, some of the information concerning it was released in 1970 by Bradley, working also in RRC.<sup>(1)</sup> Moreover, interest in glow-discharge thin films as possible dielectric materials remained, and

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in 1960 a paper concerning glow-discharge polymerization was published by Goodman, one of the nuclear battery investigators.<sup>(2)</sup> Goodman's publication appeared during the early rapid development of microelectronics research and industry, and it provoked an almost immediate interest among researchers who hoped that glow-discharge polymers as a new class of materials would play a significant role in this development. In the mid-1960's, a number of papers were published dealing either with the polymerization process itself or with electrical and more often dielectric properties of the films. In the beginning these properties were the only ones which were widely investigated, and the applications such as microcapacitors or insulating and corrosion protecting coatings were tried. The works of Bradley and Hammes,<sup>(3,4)</sup> Stuart,<sup>(5,6)</sup> Ozawa,<sup>(7)</sup> Bashara and Doty,<sup>(8)</sup> Gregor,<sup>(9)</sup> and Hirai and Nakada<sup>(10)</sup> were the most significant attempts at developing this new class of dielectrics. The early stages of research concerning the electrical properties of glow-discharge polymers have been summarized in Mearns' review.<sup>(11)</sup> Mearns, however, refers to the glow-discharge technique as one way of obtaining thin dielectric films along with other techniques such as electron bombardment of organic vapors or their exposure to UV light. It should also be mentioned here that the glow-discharge-film capacitor called Glofilm had been introduced into production in 1962, but the product's properties did not justify the costs, and production was discontinued.<sup>(1)</sup>

Once the plasma polymerization process had been discovered for its scientific interest, it began to be investigated with respect to many other possible applications. Optical, thermal, surface, biological, and permeability properties, along with the electrical properties of these films, were widely reported and corresponding applications developed. Plasma-polymerized reverse-osmosis membranes, antireflection optical coatings, corrosion protection coatings, and biocompatible materials are only a few examples. Although the development of electronic applications was a partial disappointment compared to initial hopes, the electrical properties of plasma-polymerized films continue to be the subject of extensive investigation, and the number of papers dealing with these properties surpasses those concerning other applications.

Although the plasma polymerization process is suitable for preparing either inorganic or organic thin dielectric films, the subject of this review is limited to the organic films only since the authors prefer to remain within the limits of the field of plasma polymerization recognized by most researchers. Neither was it our intention to review the state of knowledge of the plasma polymerization process itself. An ample review dealing with this process has been published by one of us recently,<sup>(12)</sup> and the purpose of this work is only to review the electrical properties of plasma-polymerized

organic films. In order to simplify the paper, it is divided into two main sections. The first section, dealing with the dielectric properties, is connected mainly with the efforts of many researchers to explain significant differences in some dielectric parameters between conventional polymers and plasma polymers and to improve the dielectric applicability of plasma-polymerized films. The second section concerns both the dark conductivity and the photoconductivity of these films and discusses the possible conduction mechanisms.

## **2. DIELECTRIC PROPERTIES OF PLASMA-POLYMERIZED ORGANIC FILMS**

### **2.1. Comparison between Dielectric Properties of Plasma-Polymerized Materials and Conventional Polymers**

As stated above, the initial hopes of rapid application of plasma-polymerized films as dielectric materials for microcapacitors did not materialize. Such hopes may have only been derived from the possibility of controlling the thickness of these films at a very low level—less than or about 1000 Å. Indeed, today we have the means of controlling the thickness of these films down to 200 Å. The thickness argument was so dominant that it overshadowed the disadvantages of other dielectric parameters of plasma-polymerized films. There are at least two factors in the dielectric characteristics of plasma polymers which make these materials less desirable compared to conventional polymers. One factor is instability of properties related to aging, and the other is dielectric loss about an order of magnitude higher than that of conventional polymers. According to Segui and Bui Ai<sup>(13)</sup> plasma-polymerized films compare well with commercial plastics with regard to dielectric strength, which usually amounts to about  $500 \text{ V } \mu\text{m}^{-1}$ , and to permittivity, which is usually  $\epsilon \approx 3$ . The dielectric loss tangents, however, are an order of magnitude higher, being in the range of  $10^{-3}$  for plasma-polymerized styrene, for instance, versus  $10^{-4}$  for conventional polystyrene.<sup>(13)</sup>

Comparison between conventional polymers and plasma-polymerized materials is of a formal nature since, from the structural point of view, they are quite different materials. This comparison, however, shows the significant features of both groups of materials. Table I compares the dielectric parameters of some conventional polymers with those of their corresponding plasma-polymerized materials. The following abbreviations are used for the plasma polymers: plasma-polymerized ethylene (PPE); plasma-polymerized styrene (PPS); plasma-polymerized isobutylene (PPIB); plasma-polymerized tetrafluoroethylene (PPTFE); and plasma-polymerized

Table I. Comparison between Dielectric Parameters of Conventional Polymers and Plasma-Polymerized Thin Films<sup>a</sup>

Conventional polymer	Dielectric constant at 20°C, 1 kHz	Loss angle tangent at 20°C, 1 kHz	Plasma polymer	Dielectric constant at 20°C, 1 kHz	Loss angle tangent at 20°C, 1 kHz	Reference
Polyethylene	2.3	0.0001-0.0002	PPE	3.57	0.0005-0.003	Tibbit <i>et al.</i> <sup>(18)</sup>
Polystyrene	2.55	0.0002	PPS	3.3	0.003	Hudis <i>et al.</i> <sup>(28)</sup>
Polyisobutylene	2.2-2.3	0.0002	PPIB	2.67	0.001-0.003	Stuart <sup>(6)</sup>
Polytetrafluoroethylene	2.0	0.0001-0.0002	PPTFE	—	0.003	Sawa <i>et al.</i> <sup>(17)</sup>
Silicon rubber filled with SiO <sub>2</sub>	3.2	0.004	PPHMDS	2.6	0.002	Morita <i>et al.</i> <sup>(26)</sup>
Poly (vinyl chloride)	3.0-3.3	0.015-0.02		3.0	0.009	Pratt <i>et al.</i> <sup>(27)</sup>
Mylar	3.1	0.005		—	0.0025	Ozawa <sup>(7)</sup>
				5.23	0.001	Tibbit <i>et al.</i> <sup>(18)</sup>
				4.98	0.003	Pratt <i>et al.</i> <sup>(27)</sup>
				4.0	0.01	Tuzov <i>et al.</i> <sup>(23)</sup>
				2.5	0.01	Brosset <i>et al.</i> <sup>(29)</sup>

<sup>a</sup> Values for conventional polymers from: J. B. Birks, *Modern Dielectric Materials*, Academic Press, New York (1960).

hexamethyldisiloxane (PPHMDS). It is seen from the Table that the dielectric constants of plasma-polymerized films are only slightly higher than those of conventional polymers, whereas the losses in plasma polymers are at least an order of magnitude higher.

Most of the conventional polymers presented in Table I are nonpolar, and the dielectric losses are extremely low in these cases. For the sake of comparison, however, the dielectric parameters for two typical polar polymers (polyvinyl chloride and Mylar) are also shown, and it is clear that their losses are also significantly higher. Plasma polymers are known to contain a certain number of polar groups<sup>(18,19,25)</sup> independent of whether the monomer used was polar or nonpolar. The presence of polar groups is without doubt one of the significant factors responsible for the relatively high (as far as polymeric materials are concerned) dielectric losses in plasma polymers.

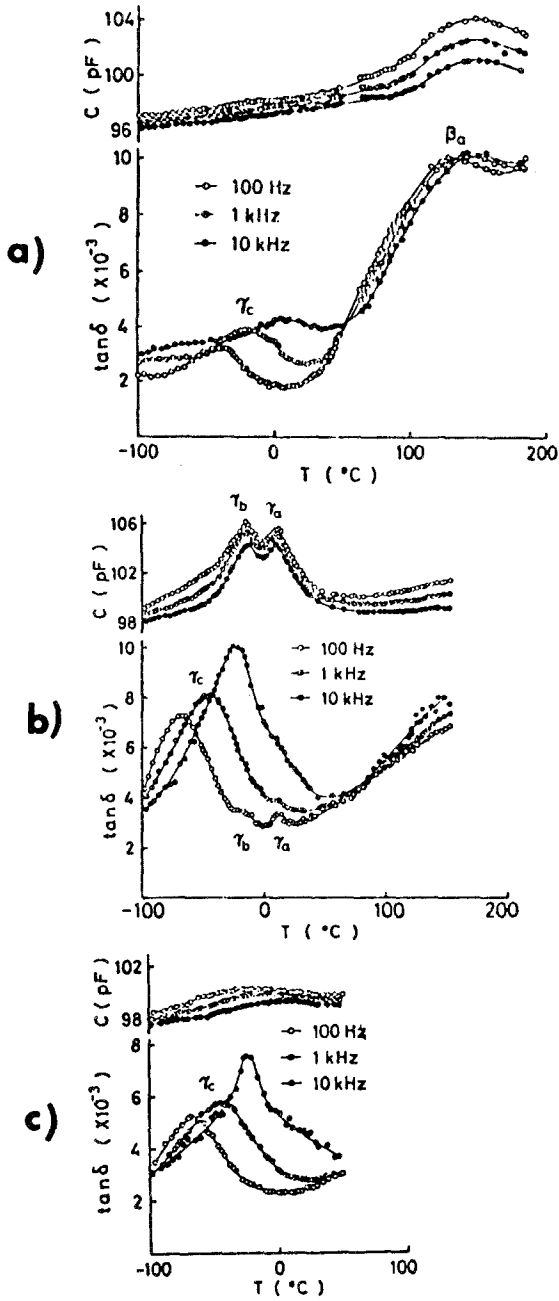
Another reason for the different dielectric behavior of plasma polymers is their very low thickness compared to conventional polymers. It is known that some dielectric parameters, especially dielectric strength, depend strongly on specimen thickness. When measuring dielectric properties of plasma-polymerized films, one operates with thicknesses around 1000 Å or less, and in this range the bulk properties of materials are already influenced by their surface properties. It has been shown, for instance, that the dielectric constant of plasma-polymerized films prepared in the same run may depend on the material used for preparation of the counterelectrode.<sup>(14)</sup>

The instability of dielectric properties of plasma-polymerized films is an even more pronounced problem. Capacitors made from these films change their capacitances with time<sup>(7,22,23)</sup> and are sensitive to humidity.<sup>(17,22,23)</sup> The aging problems are especially critical for very fresh samples which undergo significant changes within the first number of hours of exposure to ambient conditions. Thus, it is essential in every electrical measurement of plasma-polymerized films to maintain exact and reproducible conditions concerning the sample's exposure to air, humidity, and, presumably, light between their formation and dielectric measurements. The importance of such reproducibility has been stressed by Stuart.<sup>(6)</sup>

The critical influence of humidity on plasma-polymerized thin film capacitors has been followed by Ristow<sup>(22)</sup> and Tuzov.<sup>(23)</sup> Ristow introduced a parameter  $\beta_c$  indicating the relative change of capacitance per 1 % relative humidity:

$$\beta_c = (C_2 - C_1) / C_1 \text{ per } 1\% \text{ R.H.}$$

where  $C_1$  is the capacitance of a dry sample and  $C_2$  is its capacitance after water sorption. He investigated plasma-polymerized perfluorocarbons and



**Fig. 1.** Dielectric relaxation in plasma-polymerized styrene samples subjected to different moisture posttreatment. After Sawa *et al.*<sup>(17)</sup> (a, b, c) Samples 1, 2, 3.

found  $\beta_c$  to be 0.05% for perfluorocyclobutane, 0.06% for hexafluoropropylene, 0.04% for perfluoromethyldecalin, and 0.22% for perfluorobutylene. According to both Ristow and Tuzov, changes in the dielectric parameters due to humidity are reversible. Sawa,<sup>(17)</sup> however, published the results of dielectric loss increase caused by humidity in plasma-polymerized styrene, and this increase seemed to be irreversible (see Fig. 1).

It appears that both aging problems and humidity sensitivity contribute to the dielectric instability of plasma-polymerized thin films and that this instability is the major factor inhibiting the technological applications of these films.

## 2.2. Dielectric Relaxations

Most polymers contain some polar groups and, for these polymers, their dielectric behavior is a function of time and temperature. Moreover, in the case of such polymers, detailed studies of dielectric parameters such as dielectric constant and dielectric loss ( $\tan \delta$ ) over a wide range of frequencies and temperatures can provide some significant structural information. The maxima in the  $\tan \delta$  vs. temperature or frequency relationships are due to relaxation processes and can be related to either the segmental motions within the polymer chain or network or even to phase transitions such as crystallization or glass transition. It is also possible in some cases to identify polar groups which serve as tracers in these segmental motions. The distributions of relaxation times for corresponding relaxations can be calculated from  $\tan \delta$  vs. frequency relationships, and their activation energies can be calculated from  $\tan \delta$  vs. temperature relationships.

Thin polymer films obtained by means of plasma polymerization are well known to contain a certain amount of polar groups independent of the kind of monomer used in the process, and that is why they are usually suitable for dielectric relaxation studies. It is, however, much harder to relate their dielectric relaxations to the structural motions simply because their structure is not as well defined as the structure of conventional polymers. Due to their highly cross-linked nature and, as a consequence, their insolubility, very little is known about the structure of plasma polymers. In particular, the possible presence of conventional chain sequences (those which contribute to the segmental motions) in the cross-linked network is not defined at all. It is actually an academic question whether any discernible chain segments exist in a plasma polymer.

Despite all the difficulties mentioned above, an investigation of dielectric relaxations in plasma polymers can provide some structural information, and these relaxations have been reported by many researchers since the beginning of interest in plasma polymers. In one of the earliest works dealing



with plasma polymerization, Stuart<sup>(5)</sup> reported dielectric permittivity and loss tangent dependences on temperature in the range 20–120°C for plasma-polymerized styrene. In his next paper, Stuart<sup>(6)</sup> published loss tangent vs. temperature relationships in the range 20–180°C, and the relationships of the loss tangent to frequency in the range  $10^2$ – $10^5$  Hz, once again for plasma-polymerized styrene but this time mainly in mixtures with gases like oxygen and nitrogen. Ozawa<sup>(7)</sup> reported loss tangent and capacitance vs. frequency relationships in the range  $10^2$ – $10^6$  Hz for plasma-polymerized tetrafluoroethylene, and Hirai and Nakada<sup>(10)</sup> reported dielectric constant and loss tangent vs. frequency relationships in the same range for plasma-polymerized acrylonitrile. Recently, Sandved and Kristiansen<sup>(15)</sup> published both capacitance and loss angle dependences on temperature in the range 20–420°C for plasma-polymerized hexamethyldisilazane, and Phadke<sup>(16)</sup> reported dielectric constant and loss tangent vs. temperature relationships in the range 20–400°C, and vs. frequency in the range of  $6 \times 10^4$  to  $3 \times 10^7$  Hz for plasma-polymerized ferrocene. All of the papers cited above show, however, a lack of systematic studies of dielectric relaxations as well as of any significant attempt at structural interpretations.

One of the earliest attempts to relate dielectric relaxations of plasma polymers to their structural features was made by Sawa *et al.*<sup>(17)</sup> They measured the capacitance and dielectric loss of plasma-polymerized styrene as a function of temperature in the range of –100°C to +200°C. The authors interpreted the peaks appearing in their dielectric spectra by comparing their appearance temperatures as well as calculated activation energies with those of dielectric relaxations appearing in conventional polystyrene and known as peaks  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc., in order of descending temperature. For the purpose of investigating the effect of sample storage conditions after deposition, the authors prepared three different kinds of samples. Sample 1 was kept in a desiccator with silica gel, Sample 2 was exposed to water-saturated air at room temperature for 1 day, and Sample 3 was dried in vacuo for several days after being exposed to the same conditions as Sample 2.

The dielectric loss factor  $\tan \delta$  and capacitance as functions of temperature are shown in Figs. 1a–c for Samples Nos. 1–3, respectively. It is worth pointing out here that the dielectric loss tangent spectra for the originally dried sample (Fig. 1a) is almost identical with the spectra reported much earlier by Stuart,<sup>(5)</sup> also for plasma-polymerized styrene. Unfortunately, Stuart reported his relationships in the temperature range 20°C–120°C only, but his curves match very well with the same range of Sawa's plots for Sample No. 1. Extending the temperature range in both directions, Sawa *et al.* were able to record a number of relaxation peaks. The peak in loss tangent marked  $\gamma_c$  is present in the spectra of all the samples slightly below 0°C. The authors tend to relate this peak to the sorbed water peak

marked  $\gamma_2$  and observed in conventional polystyrene. A shift of temperature exists, however, placing the  $\gamma_c$  peak in plasma-polymerized styrene about 40°C higher than the  $\gamma_2$  peak in conventional polystyrene, but according to the present state of knowledge peak  $\gamma_2$  tends to shift to higher temperatures for stiffer chains, and plasma-polymerized styrene, being a highly cross-linked system, consequently exhibits an extremely stiff structure. Moreover, the activation energies of peak  $\gamma_c$  calculated by the authors for all three types of samples, 11.6, 10.1, and 10.0 kcal/mol, respectively, do not differ much among one another and are very close to the value of 12.5 kcal/mol reported for the  $\gamma_2$  peak of conventional polystyrene.

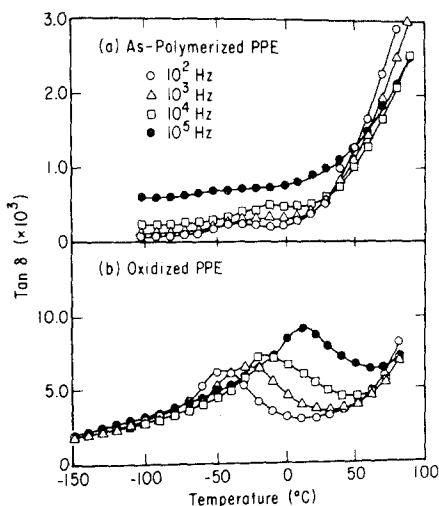
Only in the case of Sample No. 2 (Fig. 1b), which contained much more sorbed water, were the other two small peaks marked  $\gamma_a$  and  $\gamma_b$  observed in the  $\tan \delta$  spectrum next to the  $\gamma_c$  peak on its high-temperature side. The striking change of capacitance is observed, however, in the same temperatures, and the authors relate this to the large dielectric constant of water (about 80). These peaks appear almost in the same temperature where, for the conventional polystyrene, peaks  $\gamma'_1$  and  $\gamma_1$ , related to the melting of the icelike clusters and the dispersion of ice, respectively, are reported. Therefore, these two peaks in plasma-polymerized styrene have been considered by the authors to be of the same origin as in the conventional polymers.

In the higher-temperature region, a large peak in loss tangent, marked  $\beta_a$ , was observed around 130°C, as shown in Figs. 1a and b. The exposure of the sample to humid air did not cause any increase of this peak, and it was concluded that this peak is not related to the sorbed water. The  $\beta_a$  peak appears at almost the same temperature as the  $\alpha$  relaxation for conventional polystyrene, but the authors related it to the  $\beta$  type relaxation rather than to the  $\alpha$  type which, in the case of polystyrene, is connected to the glass transition. Due to cross-linking, which restricts molecular motions, it is reasonable to assume that  $\beta$  relaxation in plasma-polymerized styrene appears at a higher temperature. The same concerns the activation energy of peak  $\beta_a$ , which has been calculated to be 50.3 kcal/mole, compared to 30–40 kcal/mole reported for conventional polystyrenes.

A quite different explanation of the appearance of relaxation peaks in plasma polymers was given by Tibbitt *et al.*<sup>(18)</sup> They studied the dielectric properties of plasma-polymerized ethylene, ethylene/acetylene, ethane/vinyl chloride, and tetrafluoroethylene over the frequency range  $10^2$ – $10^5$  Hz and within the temperature range  $-150^\circ\text{C}$  to  $100^\circ\text{C}$ . The authors studied the effect of atmospheric oxygen on their films, and every sample was measured twice, first "as polymerized" and then after a certain period of exposure to the atmosphere under ambient conditions. Exposure times required to introduce noticeable changes in their dielectric spectra

differed with different materials, but the general trend was the same in each case. Being rather monotonic when taken for an "as-polymerized" sample, each characteristic exhibited a pronounced loss peak after the exposure of the samples to the atmosphere, more or less in the same temperature region. The activation energies of these peaks were found to be 13.8, 14.1, 13.5, and 12.7 kcal/mol for plasma-polymerized ethylene, ethylene/actylene, ethylene/vinyl chloride, and tetrafluoroethylene, respectively. Figure 2 shows an example of this relaxation in the case of plasma-polymerized ethylene, and Fig. 3 shows the same for plasma-polymerized ethane/vinyl chloride. Both figures show the loss tangent dependence on temperature for (a) the "as-polymerized" sample and (b) the sample after a certain time of exposure to the atmosphere.

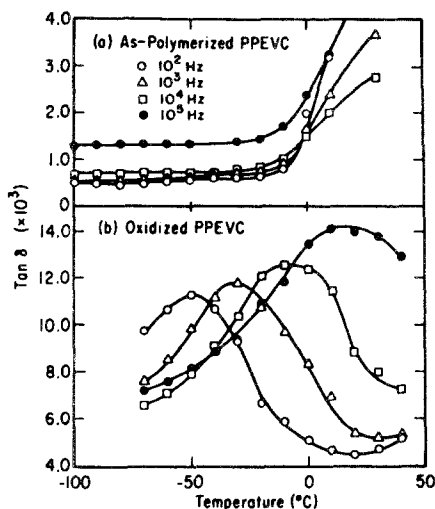
It is known that plasma-polymerized films contain considerable free radical concentration, and that most of these films show large concentrations of unsaturated double bonds as well. Plasma-polymerized ethylene is especially known to contain double bonds, while plasma-polymerized ethane/vinyl chloride contains very little unsaturation. Tibbitt's interpretation of the appearance of loss peaks in samples exposed to the atmosphere is connected with the existence of free radicals and unsaturation in these films. Atmospheric oxygen, reacting with both kinds of species, leads to extensive oxidation, resulting in the introduction of polar groups (like carbonyl or hydroxyl group) into the polymer structure, followed by the



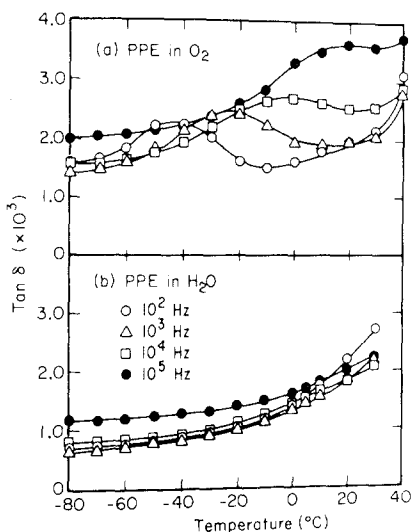
**Fig. 2.** Dielectric loss tangent as a function of temperature for plasma-polymerized ethylene. (a) As polymerized; (b) after exposure to atmosphere at ambient conditions for 190 h followed by heat treatment at 90°C for 1 h. After Tibbitt *et al.*<sup>(18)</sup>

increase of the dielectric loss. In fact, in every case discussed, the authors show the significant difference in IR spectra between "as-polymerized" films and those exposed to the atmosphere. In all three instances, there is a substantial increase of the absorption bands corresponding to the carbonyl group ( $1700\text{ cm}^{-1}$ , C=O stretching) and hydroxyl group ( $3400\text{ cm}^{-1}$ , OH stretching) after exposure. Considering the model presented above, one should not be surprised that the samples prepared from ethane/vinyl chloride mixture, which have less unsaturation, required exposure to the atmosphere for much longer times than plasma-polymerized ethylene samples (35 days compared to 190 h) in order to undergo sufficient oxidation to be reflected in the dielectric spectra. On the other hand, samples prepared by plasma polymerization of ethylene/acetylene mixture, which is known to result in even higher degrees of unsaturation than plasma-polymerized ethylene, showed significant increases in loss tangent peaks after only 68 h of exposure to the atmosphere.

Being familiar with the hypothesis presented by Sawa, Tibbitt performed an experiment to confirm or reject the role of sorbed water in the dielectric relaxation processes of his plasma-polymerized films. Plasma-polymerized ethylene samples were subjected to two different kinds of posttreatment immediately after deposition. One was exposure to pure and dried oxygen for 43 h, and the other was immersion in degassed water. The loss tangent was then measured for both samples in the range  $-80^{\circ}\text{C}$  to



**Fig. 3.** Dielectric loss tangent as a function of temperature for plasma-polymerized ethane-vinyl chloride. (a) As polymerized; (b) after exposure to atmosphere at ambient conditions for 35 days. After Tibbitt *et al.*<sup>(18)</sup>



**Fig. 4.** Dielectric loss tangent as a function of temperature for plasma-polymerized ethylene. (a) After exposure to dried oxygen for 43 h; (b) after exposure to degassed water for 43 h. After Tibbitt *et al.*<sup>(18)</sup>

40°C. The results shown in Fig. 4 indicate without any doubt that oxygen, rather than water, is responsible for dielectric relaxation in this case.

To further confirm that the carbonyl group is responsible for the recorded relaxations, the authors compared their experimental data with the Kirkwood-Froelich equation relating the macroscopic dielectric properties of polymers to their molecular parameters:

$$\Delta\epsilon = \frac{4\pi N g \mu_0^2}{3kT} \left( \frac{\epsilon_\infty + 2}{3} \right)^2 \left( \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \right),$$

where  $N$  is the number of tracer groups which in this case are assumed to be carbonyl groups, the parameter  $(g\mu_0^2)^{1/2}$  is known as the effective dipole moment of a polar group, and  $\epsilon_\infty$  and  $\epsilon_0$  are the dielectric constants at very high and very low frequencies. For their calculations, they used the data of plasma-polymerized ethylene. The relaxation strength  $\Delta\epsilon$  was determined by graphical integration of the  $\tan \delta$  vs. temperature relationship, making use of the expression

$$\Delta\epsilon = \frac{2\Delta H}{\pi R} \int_0^\infty \epsilon'' d(1/T)$$

where  $\Delta H$  is the activation energy and  $\epsilon'' = \epsilon \tan \delta$ . They assumed that  $\epsilon_0 = \epsilon_\infty = \epsilon$ , calculated  $N$  from IR data using Beer-Lambert's law, and finally obtained an effective dipole moment of 2.4 D. This value compared very well with the literature value of 2.7 D for the carbonyl group. The slight lowering of the experimental result may originate from the contribution of

the hydroxyl group dipole moment which is reported in the literature to be 1.7 D.

In the studies of the dielectric relaxations of conventional polyethylene, the  $\alpha$  relaxation has been attributed to the carbonyl groups in the oxidized polymer. According to these studies, the dielectric loss should be directly proportional to the number of carbonyl groups. Thus, Tibbitt plotted his experimental values of  $\tan \delta$  against carbonyl group contents for all his four different plasma polymers (including plasma-polymerized tetrafluoroethylene) and obtained a strictly linear relationship. This finding and the similarity in appearance temperatures as well as activation energies for the relaxations found in their four different systems allowed the authors to conclude that in each case these relaxations are related to the same mode of molecular motion driven by carbonyl tracer groups.

The concept of the carbonyl group being responsible for dielectric relaxation in plasma polymers was followed by Hetzler and Kay<sup>(19)</sup> who measured the capacitance and conductivity of plasma-polymerized tetrafluoroethylene over the wide range of frequencies from  $10^{-3}$  to  $10^5$  Hz in several different temperatures. They also found a strong absorption band at  $1725\text{ cm}^{-1}$  corresponding to the carbonyl group in the IR spectra of their samples.

The authors found that there was a strong relationship between the capacitance and conductivity of their films over the frequencies used and demonstrated their results in Cole–Cole coordinates, i.e., plotting the imaginary part of the dielectric constant  $\epsilon''$  against its real part  $\epsilon'$  with the frequency as a parameter. The quantities  $\epsilon'$  and  $\epsilon''$  were defined as

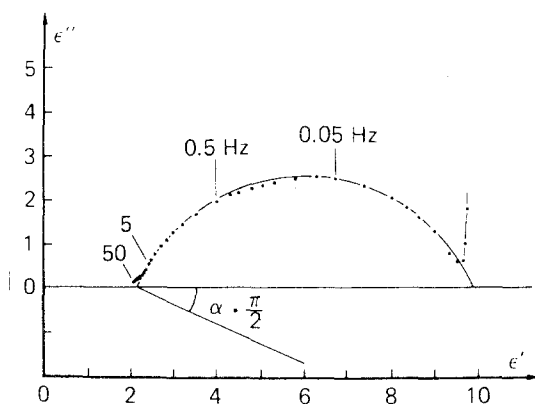
$$\epsilon' = Cd/\epsilon_0 A$$

$$\epsilon'' = \sigma/\epsilon_0 \omega$$

where  $C$  is the capacitance,  $d$  is the sample thickness,  $A$  is the electrode area,  $\sigma$  is the conductivity,  $\epsilon_0$  is the permittivity of vacuum, and  $2\pi\omega = f$ . A Cole–Cole plot for plasma-polymerized tetrafluoroethylene at  $180^\circ\text{C}$  is shown in Fig. 5. The result is not a full semicircle, and this indicates a distribution of the relaxation time. The data in Fig. 5 fit very well with the depressed semicircle in accordance with the equation:

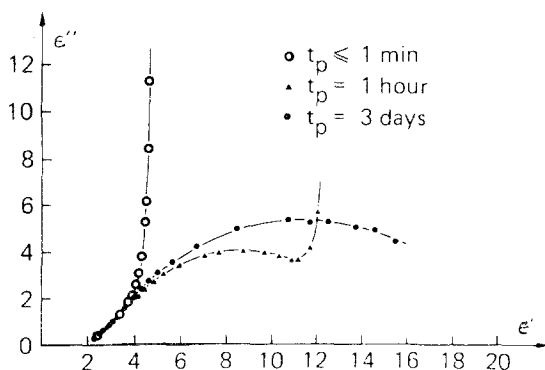
$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_{\text{HF}} + (\epsilon_{\text{LF}} - \epsilon_{\text{HF}})/[1 + (i\omega\tau)^{1-h}]$$

where  $\epsilon_{\text{LF}}$  and  $\epsilon_{\text{HF}}$  are dielectric constants at very low and very high frequencies, and  $h$  is a parameter describing the width of the distribution of the relaxation times. The data presented can be fitted well with the value  $h = 0.25$ . The deviation at very low frequency is a result of dc conductivity and becomes more pronounced at higher temperatures.



**Fig. 5.** Plots of the imaginary part,  $\epsilon''$ , of the complex dielectric constant versus the real part,  $\epsilon'$ , for plasma-polymerized tetrafluoroethylene films at 180°C with the frequency as a parameter (Cole-Cole plot). After Hetzler and Kay.<sup>(19)</sup>

In order to follow the influence of oxygen on the relaxation process, the authors performed the following experiment. Assuming that the upper electrode protects the dielectric against oxidation (slows down its rate significantly), they deposited this electrode after different times of exposure of the sample to the atmosphere. The Cole-Cole plots for three samples subjected to the different oxidation times are shown in Fig. 6. As can be seen, the sample which was exposed for the shortest possible time (less than 1 min) shows practically no relaxation and a high dc conductivity. In the second sample, which was kept exposed for 1 h, the relaxation process is



**Fig. 6.** Cole-Cole plot for three films prepared in the same run with the second electrode evaporated after different times of exposure of the samples to the atmosphere. Increasing oxidation of the films affects both the dc conductivity and the absolute increase in capacitance at low frequency. After Hetzler and Kay.<sup>(19)</sup>

already clearly developed, and the transition to dc conductivity appears at lower frequencies. The third sample, exposed to the atmosphere for 3 days, shows the full development of the Cole–Cole plot with no signs of dc conductivity, which could not be reached even for the lowest attainable frequencies. In contrast to the first two, the third sample also showed very stable behavior, indicating complete oxidation.

There are two major conclusions which can be drawn from Hetzler and Kay's work. One is that oxidation is responsible for the dielectric relaxations in plasma-polymerized tetrafluoroethylene, and the second is that there is a distribution of the relaxation times in these processes. Such distribution has been also recorded by Takeda<sup>(20)</sup> in plasma-polymerized styrene by means of the thermally stimulated current technique. He used a thermal sampling (TS) variation of the TSC technique, which makes possible the extraction of peaks due to the single relaxation time, and found at least ten such peaks in the spectrum of this sample.

Summarizing the above papers, one should point out the significance of the influence of oxygen on the dielectric behavior of plasma-polymerized materials. There are several other authors<sup>(6,16,21,24)</sup> who point out this significance. This, however, does not necessarily mean that the influence of water is negligible. There are also a number of authors<sup>(22,23)</sup> besides Sawa who emphasize the role of humidity. Although the particular relaxation peak obtained under particular conditions can be attributed to only one of these factors, it seems quite obvious in general that in the phenomenon of the instability of dielectric properties of plasma polymers both oxygen and humidity play significant roles.

### 2.3 Ways to Improve the Dielectric Properties of Plasma-Polymerized Films

The instability of dielectric parameters of plasma-polymerized materials subjected to ambient conditions as well as their significantly high dielectric losses are the two most important factors preventing the widespread application of these materials in microelectronic technologies. Thus, it is quite obvious that significant efforts are being made in order to overcome these difficulties.

Since most of the authors agree that at least part of these disadvantageous effects are due to the high free radical concentration in the films, different ways have been tried to anneal the samples after polymerization in order to decrease free radical concentration before the radicals get a chance to react with oxygen and to form polar groups. The easiest and most logical way to do this seems to be the thermal annealing posttreatment of the samples in vacuum.



The vacuum thermal treatment of plasma polymers has been tried ever since researchers first came across the problems concerning the dielectric properties of these films. It was attempted by Stuart<sup>(6)</sup> who tried to improve the dielectric stability of his plasma-polymerized styrene films by means of heat posttreatment. Unfortunately, he heated his samples up to 80°C only and reported no influence of heating. The positive results of heat treatment were first reported by Hirai and Nakada<sup>(10)</sup> who investigated plasma-polymerized acrylonitrile and tried heat-treatment temperatures between 150°C and 500°C. They obtained the best results in the case of vacuum heating in 300°C for 3 h, and these conditions allowed them to reduce the dielectric loss tangent of the samples by about 50%. Moreover, the heat-treated samples showed lower  $\tan \delta$  along the whole range of frequencies used, i.e.,  $10^2$ – $10^5$  Hz.

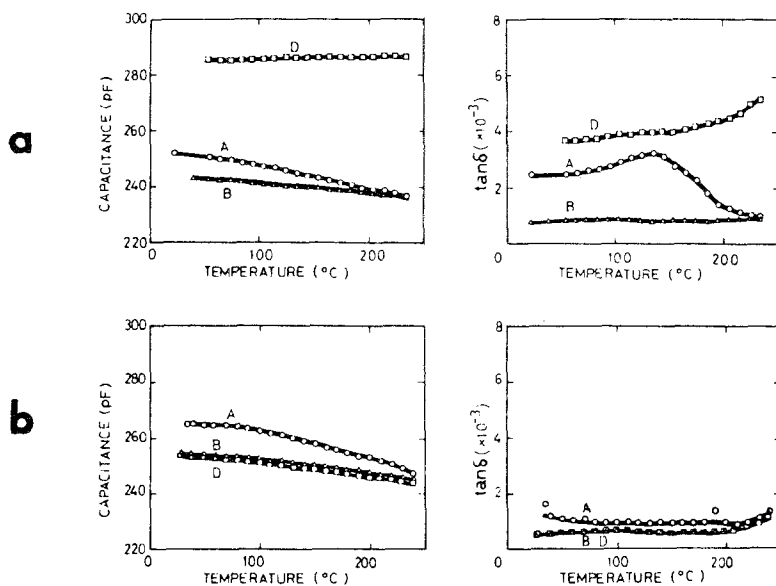
An interesting experiment concerning heat treatment has been done by Tuzov *et al.*<sup>(23)</sup> They investigated plasma-polymerized hexamethyldisiloxane samples subjected to two different heat-treatment regimes: either vacuum heat treatment in 350°C for 1 h or heat treatment at 350°C for 1 h under 1 atm of air. The stability of thin film capacitors in the humidity room was then tested over a period of 20 days. The largest capacitance increase (over 400% compared to the initial value) was observed in the case of air heat-treated capacitors which stabilized after 7–8 days. The capacitance of the untreated capacitor stabilized at about the 200% level after 4 days, and the capacitance of the vacuum heat-treated capacitors rose only to about 120% of initial value and stabilized there also after 4 days.

The influence of vacuum heat treatment on the response of plasma-polymerized thin film capacitors to relative humidity was also followed by Ristow<sup>(22)</sup> who investigated perfluorocarbon films. In the case of hexafluoropropylene, 0.5 h of 180°C heat treatment succeeded in reducing this response by about 40%, which means that the relative humidity dependence of the capacitance of the capacitor was about 40% lower for heat-treated samples. Heat treatment under the above conditions also reduced the dielectric loss tangents by about 50%.

Our own experience<sup>(27)</sup> concerning thermal annealing of plasma polymerized materials showed that films prepared from different monomers react to the vacuum thermal treatment in a different way. Among 18 monomers polymerized in low-energy conditions ( $W/FM = 10^8$  J/kg, where  $W$  is the power,  $F$  is the monomer flow rate, and  $M$  is its molecular weight), only some responded significantly to vacuum heating in 200°C for 20 min, and in only one case did heat treatment result in about 50% reduction of  $\tan \delta$  within the whole range of frequencies used, i.e.,  $10^2$ – $10^4$  Hz. We believe, however, that by changing the polymerization conditions as well as temperature and time of heat posttreatment, one can obtain

a significant reduction in loss angle tangents and an improvement in dielectric stability for most of the plasma-polymerized materials.

Heat posttreatment in vacuum has also been found by Sawa *et al.*<sup>(24)</sup> to be an effective method of stabilizing and lowering dielectric losses in plasma-polymerized styrene films. They found also, however, that similar results can be obtained by hydrogen plasma posttreatment. Sawa treated some of his samples by a hydrogen plasma of 1 Torr for 10 min immediately after deposition and then compared their dielectric properties with untreated samples. In both cases they recorded the capacitance and loss tangent changes with temperature by the following experimental procedure. First, the measurement of a fresh sample was made following heating in vacuum from room temperature to 250°C at a rate of 1.25°C/min (stage A). After the sample was kept at 250°C for 5 min, it was cooled down to room temperature. Then, the dielectric measurement was done again in the same way as for the stage A (stage B). At 250°C the sample was again kept for 5 min, this time not in vacuum but exposed to atmospheric air. After that, the chamber was evacuated once more and the sample was cooled down to room temperature. Finally, in stage D, the dielectric measurements were carried out identically as for stages A and B. The comparative results of these experiments are shown in Fig. 7. Figure 7a concerns "as-polymerized"



**Fig. 7.** Capacitance and dielectric loss tangent dependences on temperature for plasma-polymerized styrene. (a) As polymerized; (b) after hydrogen plasma treatment. After Sawa *et al.*<sup>(24)</sup>

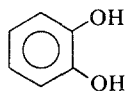
**Table II.** Dependence of the Dielectric Loss Tangent of Plasma-Polymerized Styrene/Catechol Mixture on Catechol Concentration<sup>a</sup>

	Catechol (ppm)						
	50	1000	1500	3000	5000	10,000	100,000
$\tan \delta \times 10^4$	20	23	30	22	28	24	10

<sup>a</sup> After Sar *et al.*<sup>(25)</sup>

samples not treated by hydrogen plasma, whereas Fig. 7b deals with samples subjected to hydrogen plasma just after deposition. It is seen from Fig. 7a that, similar to Tuzov's<sup>(22)</sup> results, air heat treatment raises capacitance and dielectric losses in an "as-polymerized" sample while vacuum heat treatment tends to stabilize these parameters as well as reduce them. Hydrogen plasma-treated samples, however (Fig. 7b), do not seem to be sensitive to air heat treatment at all and, independently of the stages of the experiment (A, B, or D) and temperature, show reasonably low and stable dielectric loss angle tangent, around  $\tan \delta = 0.001$ .

Quite different ways of reducing  $\tan \delta$  in plasma-polymerized styrene have been proposed by Sar *et al.*<sup>(25)</sup> Assuming that it is the unavoidable residual oxygen remaining in the vacuum chamber which is responsible for high dielectric losses in plasma-polymerized materials, they polymerized styrene in the presence of an antioxidizing stabilizer such as catechol:



Having observed that the dielectric loss of their films increases when the 50 ppm catechol content in the commercial styrene was removed before plasma polymerization, the authors followed the changes in  $\tan \delta$  with increasing concentration of this stabilizer. The results are shown in Table II. It can be seen from this table that at low concentrations, up to 10,000 ppm, the effect is almost nonexistent and, strictly speaking, negative. A concentration of 1500 ppm of catechol results in a 50% increase in  $\tan \delta$ . A high concentration of catechol (100,000 ppm), however, causes a significant drop in  $\tan \delta$ .

The second method of  $\tan \delta$  reduction proposed by Sar is based on calculations showing that the decrease of the gap between the electrodes in the glow discharge results in the lowering of the mean kinetic energy of the ions. This is followed, in consequence, by decreasing free radical concentration in the finally deposited film. The results of  $\tan \delta$  measurements for different distances between the electrodes are given in Table III. The

**Table III.** Dependence of the Dielectric Loss Tangent of Plasma-Polymerized Styrene on the Distance between Electrodes<sup>a</sup>

Pressure (Torr)	Distance (mm)	$\tan \delta \times 10^4$
0.3	50	33-40
	40	20-30
	30	20-25
	30	19-23
0.6	20	12-16
	10	9-13
2.5	7	7-10

<sup>a</sup> After Sar *et al.*<sup>(25)</sup>

gap decrease also resulted in a significant increase of glow-discharge pressure, which is also specified in the table. It is evident from this table that by manipulating the experimental setup one can reduce the dielectric losses in plasma-polymerized styrene by a factor of 4-5.

Among the cited methods of improving the dielectric properties of plasma-polymerized materials, vacuum heat treatment seems to be the most widely tried and the most effective. Hydrogen plasma treatment as well as optimization of the discharge zone geometry are, however, also very promising attempts. The most doubtful method is the introduction of catechol to the discharge. First, a significant response in the desired direction has been obtained with a catechol concentration as high as 10%, while in the case of lower concentrations the results seemed to be either randomly spread or even show the reverse tendency. Second, the catechol (especially at such high concentrations) may have reacted as a comonomer and changed the polymerization mechanism rather than acting as an oxygen scavenger only.

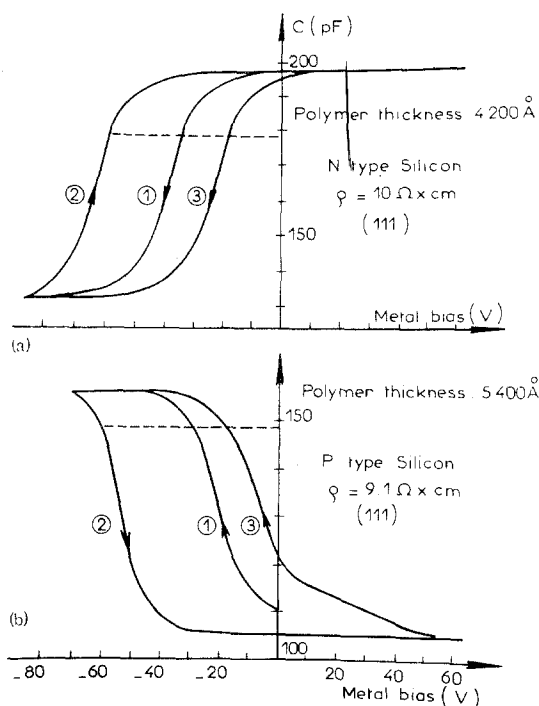
## 2.4. Properties of Metal-Plasma Polymer-Semiconductor Structures

One of the potential applications of plasma-polymerized organic films in microelectronics besides the production of microcapacitors is the deposition of passivation layers onto semiconductor devices. A good passivation layer must fulfill two requirements: it should shield the device from outside influence but should not interrupt its operation at the same time.<sup>(13)</sup> Classically applied layers involve deposition of SiO<sub>2</sub> obtained by thermal oxidation. This technique is not suitable, for instance, for III-V group component semiconductors such as gallium arsenide since it requires temperatures above the decomposition point of the semiconductor itself.<sup>(29)</sup> Since plasma-polymerized organic films have other advantages over thermally deposited SiO<sub>2</sub>, such as lower permeability to alkaline ions and lower sensitivity to

radiation,<sup>(30)</sup> significant effort has been made recently to develop this application.

Passivation of semiconductor devices by plasma polymers involves the electrical properties of the semiconductor-polymer contact. Thus, it is not surprising that a great deal of attention has been paid to these properties in the last decade and a number of publications have appeared dealing with the characteristics of MPS (metal-plasma polymer-semiconductor) structures.<sup>(29-35)</sup> Most of the work cited dealt with different types of silicon as semiconductor, but other semiconductors such as GaAs have also been used.<sup>(29)</sup>

The usual method of investigating MPS structure is to follow the capacitance change with the change in a very low frequency bias voltage ( $10^{-3}$ – $10^{-1}$  Hz) superimposed onto the working voltage of high frequency. Such an experiment allows one to plot  $C(V)$  curves using different sweep rates. A typical  $C(V)$  behavior of MPS structures for both  $n$ -type and  $p$ -type silicon and plasma-polymerized styrene as presented by Sanchez *et al.*<sup>(31)</sup> is shown in Fig. 8. It can be seen from the figure that the  $C(V)$



**Fig. 8.** Typical  $C(V)$  behavior of metal-polymer-semiconductor structures. Plasma-polymerized styrene as dielectric. Experimental conditions: temperature  $25^\circ\text{C}$ ; signal  $3 \times 10^4$  Hz; bias sweep 0.05 Hz. (a)  $n$ -type silicon; (b)  $p$ -type silicon. After Sanchez *et al.*<sup>(31)</sup>

characteristic exhibits a strong hysteresis phenomenon. An explanation of this phenomenon has been given by Maisonneuve *et al.*<sup>(34)</sup> who investigated MPS structures with plasma-polymerized hexamethyldisiloxane as the dielectric. According to this explanation, the hysteresis cycle is attributed to the aggregation of high-mobility carriers (i.e., electrons or holes) at the semiconductor–dielectric interface. At first these carriers result from the interface exchange only. However, when the space charge due to the positive ions is created, the electrons in the dielectric begin to move and also contribute to the effect. The authors estimated the mobility of the carriers responsible for the hysteresis cycle by performing the following experiment: after the sample had been polarized in a high field, a pulsed voltage of variable amplitude and duration was applied, and the capacitance of the sample was followed. When the maximum and minimum values of capacitance are obtained for a given pulse, the duration of the pulse corresponds to the carriers' transfer from one contact to the other. Knowing then the thickness of the sample, one can calculate the mobility of the carriers using the equation:

$$v = \mu E$$

where  $v$  is the linear speed of the carriers,  $\mu$  is the mobility of the carriers, and  $E$  is the electric field. In the case of a 2600 Å thick film of plasma-polymerized hexamethyldisiloxane, the pulse required to shift the capacitance from the maximum to the minimum values had an amplitude of 60 V and a duration of 50 ms. The value of the carrier mobility estimated from the above data is  $3 \times 10^{-10} \text{ cm}^2/\text{V s}$  and is of the same order of magnitude as the mobilities of electrons usually found in thin polymer films.

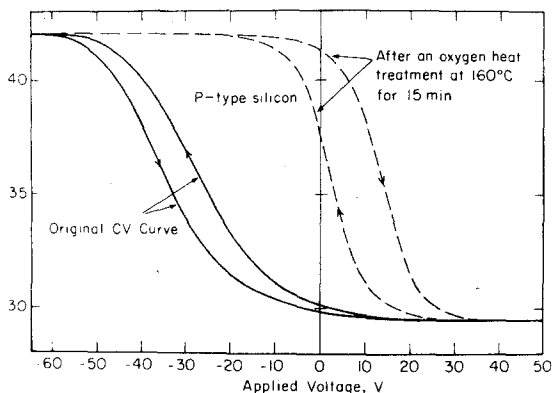
Although the high-mobility carriers are responsible for the hysteresis cycles in the  $C(V)$  characteristics of MPS structures, they are not the only kind of carriers detectable by this technique. When a high stationary external positive field (about 2 MV/cm) was applied to silicon–polysiloxane–gold structures,<sup>(34)</sup> the successively recorded  $C(V)$  characteristics kept shifting for a relatively long time approaching several hours. The explanation given by Maisonneuve is that the low-mobility carriers (which are regarded as positive ions) located at the metal–polymer interface keep drifting under the influence of the external field until they reach the opposite, polymer–semiconductor contact. On the basis of the time required for the new equilibrium to be reached, the mobility of these carriers has been estimated to be of the order of magnitude of  $10^{-16} \text{ cm}^2/\text{V s}$ .

As far as the technological application of plasma-polymerized passivation layers for semiconductor devices is concerned, the above phenomena (i.e., the existence of hysteresis as well as its shift under the influence of

the external field) are, of course, disadvantageous from the practical point of view. Thus, attempts have been made to reduce these effects by different kinds of treatments. Once again, heat treatment in a neutral atmosphere was the most successful. Maisonneuve *et al.*<sup>(32)</sup> annealed their silicon-plasma polymerized siloxane samples in a nitrogen atmosphere for 10 h at 450°C before applying the upper, metal electrode. The effect was significant: they succeeded in reducing the width of the hysteresis cycle by about an order of magnitude from 12 to 1–2 V. The shift of the  $C(V)$  curve was also significantly reduced, indicating that the density of ion structures also decreased as a result of heat treatment.

Whereas inert gas heat treatment improves the  $C(V)$  properties of plasma-polymerized films, oxygen heat treatment, again, seems to work in the opposite direction. Szeto and Hess<sup>(35)</sup> reported  $C(V)$  curves for plasma-polymerized tetramethylsilane films before and after such treatment (Fig. 9). The result of this experiment when correlated with the other oxygen treatment experiments<sup>(22,24)</sup> indicates that after oxygen heat treatment the electrical properties of the film become dominated by polarization effects, thus reversing the hysteresis direction.

Two major conclusions drawn from the above studies are as follows: first, the presence of both electronic as well as ionic charge carriers in plasma-polymerized organic films has been detected by means of capacitance-voltage measurements, and second, it has been shown that the technological use of these films as passivation layers for semiconductor devices can be significantly improved by heat annealing in an inert gas atmosphere.



**Fig. 9.** Capacitance versus voltage plots for plasma-polymerized hexamethyldisiloxane films. Solid trace represents as-polymerized sample and the dotted trace represents the same sample after oxygen heat treatment. After Szeto and Hess.<sup>(35)</sup>

## 2.5. Dielectric Breakdowns in Plasma-Polymerized Thin Films

The dielectric strengths of plasma-polymerized materials are difficult to compare in a systematic manner since the breakdown voltage of a thin film does not increase linearly with thickness. The dielectric strength results for plasma-polymerized perfluorocyclobutane samples of different thicknesses published by Pachonik and Seebacher<sup>(36)</sup> are presented here in Table IV.

The breakdown voltage of plasma-polymerized films also strongly depends on the method of carrying out the breakdown experiment, especially on the area of the electrodes of the sandwich-type sample. Sapiuha *et al.*<sup>(37)</sup> in their investigation of breakdown spots in plasma-polymerized films distinguish four different types of breakdown dependent on the experimental conditions:

1. Destructive
2. Propagating self-healing
3. Single-hole self-healing
4. Nondestructive

The first three kinds of breakdown are significant from the technological point of view. The first two determine the dielectric strength of the film, and the third provides a convenient way of improving this parameter by eliminating weak spots from the dielectric. Weak spots are the areas of the sample exhibiting lower dielectric strength on which the initial breakdowns take place. Their nature is not fully understood, and their appearance may be connected with factors such as the microinhomogeneity of the film or the local roughness of the electrode surface, for instance.<sup>(38)</sup> Single-hole self-healing breakdown is a method of eliminating such weak spots since the very local overheating of the electrode material causes its evaporation if its thickness is sufficiently small (usually smaller than 1500 Å) and the short-circuit is opened again. Perhaps the best illustration of such self-healing breakdowns which improve the dielectric strength of the film is

**Table IV.** Values of Electric Field Necessary to Break Down Plasma-Polymerized Perfluorocyclobutane Samples of Different Thicknesses<sup>a</sup>

	Thickness (nm)		
	150	100	75
Electric field ( $\text{V } \mu\text{m}^{-1}$ )	450–550	550–650	700–800

<sup>a</sup> After Pachonik and Seebacher.<sup>(36)</sup>



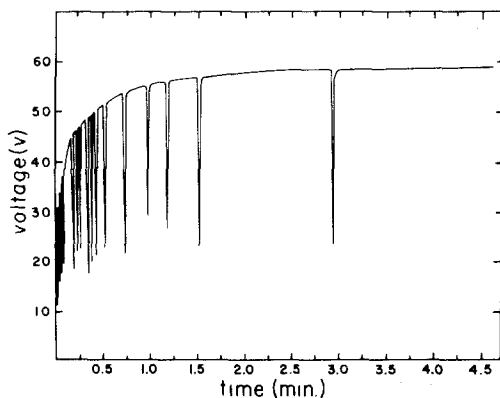


Fig. 10. Variation of breakdown voltage with successive breakdowns for 1500 Å thick sample of plasma-polymerized methyl methacrylate. After Sapieha *et al.*<sup>(39)</sup>

given by Sapieha *et al.* in Ref. 39. They used a 1500 Å film of plasma-polymerized methyl methacrylate with an evaporated upper aluminum electrode only 100 Å thick. The breakdown voltage following successive breakdowns of the sample is shown in Fig. 10. It is seen that after such a self-healing clearance process the dielectric strength of the sample reaches its final stable value, which in the cited example is 390 V/μm. Moreover, the sample behaves in a stable manner in the next sweeps as well.

As was mentioned before, in one of his other papers, Sapieha *et al.* investigated the different types of breakdown in terms of the morphological properties of the breakdown spot (or channel) which depend on the breakdown energy.<sup>(37)</sup> Sapieha studied plasma-polymerized styrene and benzene

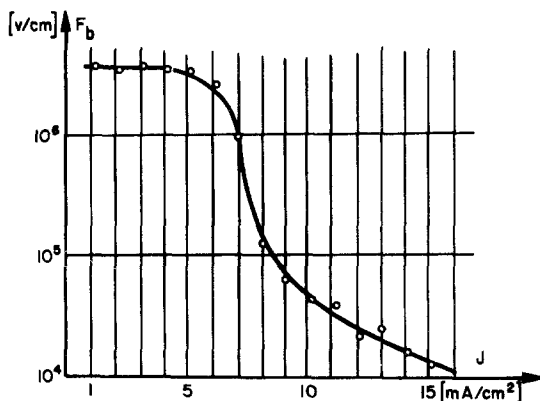


Fig. 11. Dependence of the electric field at breakdown on the glow-discharge current density for plasma-polymerized styrene. Sample thickness  $3750 \pm 250$  Å. After Sapieha and Kryszewski.<sup>(38)</sup>

samples and found that for energies lower than  $10^{-5}$  J nondestructive breakdown took place. At higher energies partial destruction of the breakdown channel occurred, and a complete, single-hole self-sealing breakdown required an energy level of at least  $5 \times 10^{-3}$  J.

Sapieha is one of the few researchers who investigated dielectric breakdown in plasma-polymerized thin films and reported the relationship between the dielectric strength and the energy conditions of sample preparation in the plasma polymerization process itself.<sup>(38)</sup> Figure 11 presents this relationship for plasma-polymerized styrene samples of thicknesses  $3750 \pm 250$  Å. Here the glow-discharge current density reflects the energy input during the plasma polymerization, and it is shown that low-energy conditions are preferable from the point of view of the dielectric strength of plasma polymers.

### 3. ELECTRICAL CONDUCTION IN PLASMA-POLYMERIZED ORGANIC FILMS

#### 3.1. Dark Conductivities of Plasma Polymers

Plasma-polymerized thin organic films, being in general dielectric materials, show extremely low conductivities, placing them among insulators. This was first reported by Bradley and Hammes<sup>(3)</sup> who published in 1963 a long list of dc electrical conductivities of thin films that were plasma polymerized from a variety of monomers. These conductivities, shown in Table V, were measured at two different temperatures, 150°C and 250°C, so that the respective thermal activation energies of conduction were also calculated. As can be seen, the absolute values of the dark conductivities at 150°C vary between  $10^{-18}$  and  $10^{-13}(\Omega \text{ cm})^{-1}$ . Most values, however, are in the range  $10^{-16}$ – $10^{-14}(\Omega \text{ cm})^{-1}$ , and activation energies in this group are usually close to 1.36 eV. Among those exhibiting higher conductivity values, there are a few films containing sulfur, some polymers containing nitrile groups, and plasma-polymerized ferrocene. It appears that in these cases the conduction mechanism may be different compared to plasma polymerized hydrocarbons and other compounds which exhibit lower conductivity. The activation energies for the films belonging to the higher conductive group are significantly lower, never exceeding 0.9 eV. Nitrile groups as well as sulfur or iron atoms probably dominate conduction, thus lowering the resistivity of the films. Our own experience concerning sulfur-containing films<sup>(27)</sup> indicates that these films show higher dielectric losses than any other group investigated, and we explain this observation in terms of the favorable charge-transfer characteristic of sulfur.

**Table V.** Typical Conductivity Data for Plasma-Polymerized Materials<sup>a</sup>

Monomer	$\sigma$ (mho/cm)		$E_a$ , eV
	150°	250°	
Naphthalene	$9 \times 10^{-16}$	$2.7 \times 10^{-13}$	1.1
Styrene	$6 \times 10^{-16}$	$9 \times 10^{-14}$	1.2
<i>p</i> -Xylene	$5 \times 10^{-17}$	$1.5 \times 10^{-13}$	1.8
Cyclopentadiene	$1.0 \times 10^{-16}$	$1.2 \times 10^{-13}$	1.5
Hexamethylbenzene	$7 \times 10^{-17}$	$7 \times 10^{-14}$	1.5
Ethylene oxide	$4 \times 10^{-16}$	$1.6 \times 10^{-13}$	1.1
Methoxynaphthalene	$1.1 \times 10^{-16}$	$7 \times 10^{-14}$	1.5
Thiourea	$3.3 \times 10^{-16}$	$4 \times 10^{-13}$	1.7
Chlorobenzene	$8 \times 10^{-17}$	$1.9 \times 10^{-14}$	1.4
Picoline	$2.2 \times 10^{-14}$	$6 \times 10^{-12}$	1.1
<i>N</i> -Nitrosodiphenylamine	$8 \times 10^{-15}$	$3.0 \times 10^{-12}$	1.2
<i>p</i> -Toluidine	$7 \times 10^{-16}$	$2.3 \times 10^{-12}$	1.5
Aniline	$2.8 \times 10^{-16}$	$1.4 \times 10^{-12}$	1.8
<i>p</i> -Nitrotoluene	$5 \times 10^{-16}$	$2.5 \times 10^{-13}$	1.2
Diphenyl selenide	$3.1 \times 10^{-18}$	$8 \times 10^{-13}$	0.75, 1.5
Diphenyl mercury	$2.8 \times 10^{-15}$	$2.7 \times 10^{-13}$	0.85
Ferrocene	$2.7 \times 10^{-13}$	$4.5 \times 10^{-12}$	0.55
Benzene selenol	$2.5 \times 10^{-14}$	$7 \times 10^{-12}$	1.1
Hexa- <i>n</i> -butylditin	$1.5 \times 10^{-15}$	$7 \times 10^{-13}$	1.1
Tetracyanoethylene	$1.8 \times 10^{-13}$	$5 \times 10^{-12}$	0.60
Malononitrile	$3 \times 10^{-14}$	$1.8 \times 10^{-12}$	0.75
Thianthrene	$1.5 \times 10^{-14}$	$1.6 \times 10^{-12}$	0.85
Thiophene	$6 \times 10^{-14}$	$3 \times 10^{-12}$	0.75
Thioacetamide	$8 \times 10^{-14}$	$9 \times 10^{-12}$	0.85

<sup>a</sup> Typical thickness of the specimen  $1.5 \pm 0.5 \mu\text{m}$ , applied voltage 1.4 V. After Bradley and Hammes.<sup>(3)</sup>

It has to be mentioned here that there was significant success in increasing the dark conductivities of some plasma polymers reported by Hirai and Nakada.<sup>(10)</sup> The dark conductivity of plasma-polymerized acrylonitrile, which is in the range  $10^{-17}$ – $10^{-16} (\Omega \text{ cm})^{-1}$ , can be increased as much as about ten orders of magnitude by prolonged (3 h) vacuum heating at temperatures up to 500°C. Heat treatment is not, however, the universal means of increasing the conductivity. Bradley,<sup>(51)</sup> for instance, reported frequent decreases of dark currents after prolonged measurements at 180°C or above.

The list presented in Table V does not include some of the monomers which have been studied intensively in recent years such as tetrafluoroethylene (or generally Freons) and organosilicones. For the sake of comparison, we present here the respective values of conductivities for materials polymerized from the above monomers. As far as plasma-polymerized tetrafluoroethylene is concerned, Vollman and Poll<sup>(40)</sup> reported conductivity

values in the range  $10^{-17}$ – $10^{-18}$  ( $\Omega \text{ cm}$ ) $^{-1}$ . Hetzler and Kay<sup>(19)</sup> studied the ac conductivities of the films obtained from the same monomer and reported conductivities between  $10^{-15}$  and  $10^{-10}$  ( $\Omega \text{ cm}$ ) $^{-1}$  for the frequency range  $10^{-3}$ – $10^5$  Hz. For very low frequencies, however, a leveling out to the dc conductivity was found, and the calculated value of this conductivity,  $\sigma = 10^{-17}$  ( $\Omega \text{ cm}$ ) $^{-1}$ , was in good agreement with Vollman and Poll's data, both corresponding to room temperature. The same order of magnitude of dc conductivities at room temperature can be calculated from several  $I(V)$  characteristics published by Kryszewski *et al.*<sup>(41)</sup> and Tyczkowski *et al.*<sup>(42)</sup> for plasma-polymerized organosilicones and particularly polysiloxanes and polysilazanes. Szeto and Hess<sup>(43)</sup> presented similar characteristics for plasma-polymerized tetramethylsilane films, and the conductivity data calculated from their plots are slightly higher:  $10^{-15}$ – $10^{-16}$  ( $\Omega \text{ cm}$ ) $^{-1}$ . A similar conductivity value of  $10^{-15}$  ( $\Omega \text{ cm}$ ) $^{-1}$  was also reported by Brosset for plasma-polymerized hexamethyldisiloxane films.<sup>(29)</sup> When comparing the above values of dc conductivity with the data in Table V, however, one has to keep several points in mind. First, Bradley and Hammes' data concern conductivities at higher temperatures, i.e., 150°C and 250°C, and the values extrapolated to room temperature should be at least one order of magnitude lower. Second, dc conduction in the above materials is usually not an ohmic phenomenon, with currents decreasing with time, and consequently all the conductivity values are field and time dependent. Finally, the properties of plasma-polymerized films depend on the deposition parameters and may also be dependent on the geometrical characteristic of the equipment; thus comparisons of data obtained by different authors may sometimes be misleading.

Plasma polymerization of organometallic monomers may be a good example of the need for such special care when discussing electrical properties. Among the monomers presented in Table V, there are some organometallic compounds, namely diphenylmercury, ferrocene, or hexa-*n*-butylditin, and the conductivities of their films are low enough to place them among insulators. Recently, however, a number of papers appeared dealing with properties of plasma-polymerized organotin and organogermanium films<sup>(44–48)</sup> showing that, depending on the deposition conditions, these properties may vary from insulating through semiconducting to even conducting. Studies concerning plasma-polymerized organometallic films have been carried out for a number of years at the University of Missouri-Rolla by a team led by W. J. James. The above cited papers constitute the result of these studies. In Refs. 44 and 45 Kny *et al.* reported the variety of products plasma polymerized from tetramethyltin in a tubular flow reactor powered by RF. The decisive experimental factor in these studies was the geometrical factor: sample position along the reactor. Both the visual appearance and the properties of the films depended strongly on this

factor. Metallic films with a carbon-to-tin ratio between 1 and 2.5 and conductivity values of  $10^{-1}$ – $10^{-2} (\Omega \text{ cm})^{-1}$  were obtained in certain positions, while insulating, transparent films were deposited in the others. The conductivity of the semiconductive films increased reversibly with temperature, but above a certain threshold value ( $106^\circ\text{C}$ ), the changes seemed to be irreversible and values up to  $10^2 (\Omega \text{ cm})^{-1}$  were obtained by prolonged treatment at this temperature. The work continued in the papers of Sadhir *et al.*<sup>(46–47)</sup> was then accomplished by introducing oxygen into the reaction chamber. Films deposited by plasma polymerization of organotin and oxygen mixtures exhibited conductivities up to  $10^4 (\Omega \text{ cm})^{-1}$ . At a certain point, however, with sufficiently low carbon-to-tin ratio, these films began to show clearly metallic behavior of decreasing conductivity with increasing temperature. Electron diffraction, x-ray diffraction, and DTA data of such highly conductive products indicated without doubt that they possessed the  $\beta$ -tin structure. Since elemental analysis still showed some remaining carbon content, the  $\beta$ -tin structure with carbon in the interstices was proposed for these materials. The boundary between organic and inorganic structure is not sharp in this case, and thus care should be taken when speaking of “organic film” conductivity. Nevertheless, we have discussed these materials here because they provide a very good illustration of the fact that not only do the structure and properties of plasma-polymerized films depend strongly on the polymerization conditions but even their general classification as organic or inorganic materials may vary with these conditions.

Very recently, the synthesis of organogermanium films in a glow discharge was also reported by the same team.<sup>(48)</sup> The highest conductivities for these films, obtained from tetramethylgermanium, were about  $10^{-6} (\Omega \text{ cm})^{-1}$ . This value, although much lower than in the case of organotin films, is still about seven orders of magnitude higher than the highest conductivities shown in Table V.

### 3.2. Bistable Switching in Plasma-Polymerized Films

Switching or memory-type phenomena are usually observed in a variety of inorganic materials such as certain metal oxides or amorphous semiconductors. Reports concerning these phenomena in polymer films are rare; nevertheless a number of papers have been published reporting switching in plasma-polymerized organic films as well.<sup>(9,49,50)</sup> It was Gregor in 1968 who first reported an unusual behavior of his plasma-polymerized divinylbenzene and styrene samples.<sup>(9)</sup> He observed a sudden increase in conductivity of the samples when the applied dc voltage was raised, but only when the specimen thickness did not exceed 300 Å. The high-conductivity region

(the "on" state), however, was not stable in Gregor's case, and the conductivity became "normal" (the "off" state) again when the voltage was raised. Nevertheless, the phenomenon was reproducible (Gregor reported as many as 250,000 switches on a single sample), and what is even more important is that it was also reversible, i.e., switching was also observed with the opposite polarity of the sample.

Truly bistable switching in plasma-polymerized films has been reported at least twice by French researchers from Paul Sabatier University in Toulouse led by Segui and Bui Ai.<sup>(49,50)</sup> They investigated plasma-polymerized styrene and found two electrically distinct states in their structures. The observed ratio of resistances between the "on" (low-resistance) and "off" (high-resistance) states amounted to a value as high as  $10^7$ . The initial state of each sample was always the "off" state. When the sample was subjected to increasing electric field, a switch toward the "on" state was observed at a certain threshold voltage. This state was stable even after removal of the field. The return transition to the "off" state could be achieved by applying a pulse of several volts.

One of the possible causes of the observed switching could be the formation of a metal bridge between the electrodes due to the local overheating and melting of the electrode material (either gold or aluminum) which could then diffuse through the polymer films. The switching phenomenon would be then an artifact not reflecting the properties of the polymer itself. In order to support or reject electrode diffusion as being responsible for the switching, Segui *et al.*<sup>(50)</sup> performed an experiment in which both electrodes consisted of polished, solid tungsten. The film was deposited on the lower electrode, and the upper electrode was applied by means of pressure. The melting point of tungsten is  $3410^\circ\text{C}$ , and it is believed that tungsten cannot melt and penetrate the polymer film. The switching in the tungsten sandwiched samples had the same characteristic as that for gold electrodes, and the electrode diffusion hypothesis was thus excluded.

The other possible explanation of such a switching behavior was the formation of an amorphous carbon path through the film. This hypothesis was especially interesting since each switch from the "off" to the "on" state was accompanied by sparking. After the sample was switched to the "on" state, however, the sparks did not appear.

As was mentioned before, the switch from the "on" to the "off" state was achieved by applying a pulse of several volts. Segui *et al.*<sup>(50)</sup> performed a quantitative analysis of this transition based on the balance equation for the heat necessary to evaporate a conductive carbon filamentary path. The thermal energy was supplied by the pulse according to the relation

$$E = VIt_d$$

where  $V$  is the voltage across the sample,  $I$  is the current flowing through the sample, and  $t_d$  is the duration of the pulse. This amount of heat is used to evaporate the carbon path according to the equation

$$C_v(T_m - T_0)v\mu + L_v\mu = E$$

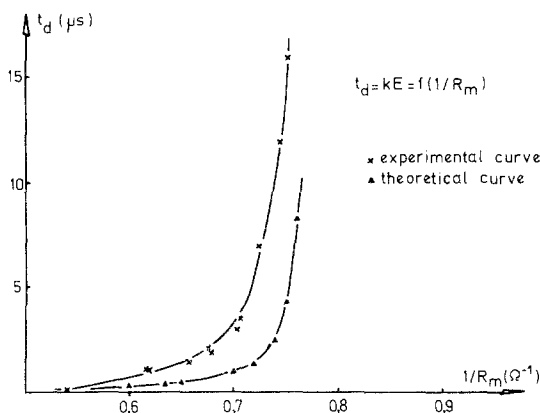
where  $C_v$  is the specific heat,  $T_m$  is the sublimation temperature of amorphous carbon,  $\mu$  is the specific mass of the channel material, and  $L_v$  is the latent heat of vaporization. The channel volume  $v$  may be expressed in terms of the measured resistance  $R_m$ :

$$v = \frac{\delta l^2}{1 - R_0(1/R_m)} \frac{1}{R_m}$$

where  $\delta$  is the resistivity of the path,  $l$  is its length, and  $R_0$  is the part of  $R_m$  due to the contact. Rewriting the above equations and making the necessary assumptions concerning the material constituting the path (with the basic assumption that it is amorphous carbon), the authors arrived at the final equation of energy equilibrium:

$$[C_v(T_m - T_0) + L_v] \frac{l^2 \delta}{1 + R_0(1/R_m)} \frac{1}{R_m} = \frac{V^2}{R_0 + R_d} t_d$$

where  $R_d$  is the value of the additional resistance used in series with the sample in the experiment. The above equation involves only measurable variables or constant parameters and may be written as the function  $t_d = f(1/R_m)$ , which exhibits a vertical asymptote at  $1/R_0$ . Figure 12 shows a



**Fig. 12.** Delay time for the “on” to “off” transition versus reciprocal of the resistance for plasma-polymerized styrene. Comparison between experimental results and theoretical data obtained with the assumption of evaporation of the conductive carbon path. After Segui *et al.*<sup>(50)</sup>

comparison between the data obtained from this equation and the experimental results in  $t_d$  versus  $1/R_m$  coordinates.

The above procedure may be applied with the assumption that the conducting paths are built out of gold (electrode material). The calculated theoretical values for such a case can be obtained by multiplying  $t_d$  in Fig. 12 by a factor of  $2 \times 10^{-3}$ , and it is obvious that the disagreement with experimental data forces one again to exclude the gold path as being responsible for switching in this case. Conversely, agreement between theoretical and experimental values for the assumed carbon path is sufficient to draw the following conclusions summarizing the phenomenon of bistable switching in plasma-polymerized styrene films:

1. The switch from the low-conductive "off" state to the high-conductive "on" state occurs via local degradation of polymer and formation of highly conductive amorphous carbon paths through the thickness of the film.
2. The reverse switch from the "on" state to the "off" state is performed by applying a pulse sufficient to evaporize carbon and to destroy the paths.

The above model of bistable switching involves the evolution of gaseous hydrogen during the formation of a carbon tunnel (switching from the "off" to the "on" state). Indeed, a hydrogen peak has been found in a gas chromatogram of the gas phase surrounding the sample after such switching, constituting further confirmation of the model.

It is also important to point out here that the bistable switching presented above has nothing to do with any kind of dielectric breakdown described in Section 2.5, and it is believed that its usefulness will be shown in the future.

### 3.3. Photocurrents and Photoconductivity

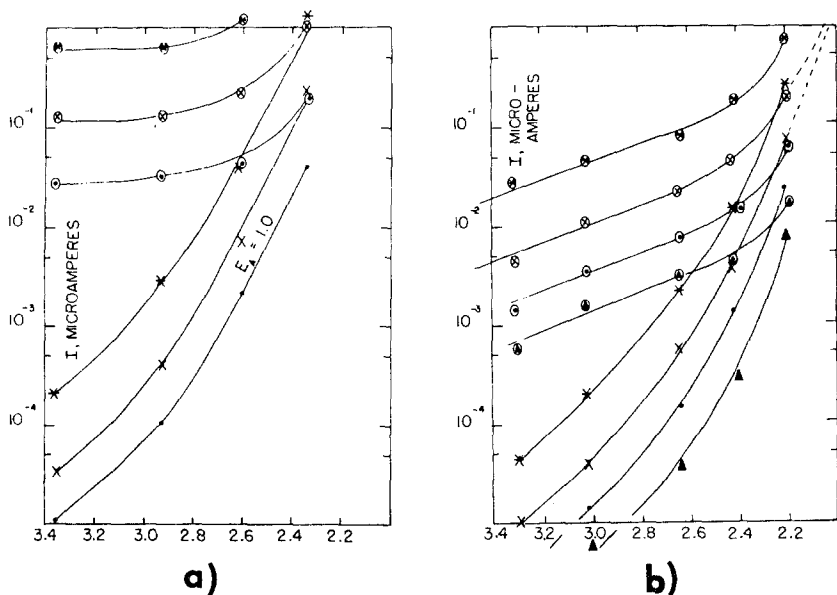
Since the beginning of interest in the electrical properties of plasma-polymerized organic films, the dc conductivity of such materials has been recognized as light sensitive. It was Bradley, again, who first reported this finding.<sup>(4,51)</sup> Since then, however, photoconduction has not gained much attention, and only a few papers have been published.<sup>(10,52-55)</sup>

In the first paper concerning photoconduction, Bradley and Hammes chose films exhibiting relatively high dark conductivities and reexamined them, this time subjecting them to illumination from a tungsten-filament white light source.<sup>(4)</sup> The main group of these films contained either nitrogen or sulfur, but other materials, such as plasma-polymerized ferrocene or plasma-polymerized diphenyl selenide, were also examined. An additional



current under light excitement was a general property of all the films studied. Good examples of such additional photocurrents measured in the temperature range 25–175°C are shown in Fig. 13 for plasma-polymerized thioacetamide (a) and plasma-polymerized pyrazole (b). As can be seen in the figure, in each case the thermal activation energy for dark and photoconductivity differs significantly, the latter being usually three to four times smaller. This means that in all cases dark conductivity increases faster with temperature than photoconductivity, and the gain of current due to light excitation is more pronounced at lower temperatures. The example of plasma-polymerized thioacetamide (Fig. 13a) describes well the above statement. At room temperature the photo-to-dark current ratio is 2500:1, but it decreases to about 200:1 at 90°C and only 5:1 at 150°C.

The interesting phenomenon found by Bradley and Hammes was that all their specimens showed residual zero-voltage currents, with the photo-to-dark ratios and the temperature dependence being identical to those obtained with an applied field (see example in Fig. 13b). The light-induced, self-generated currents usually result from photovoltage, the emf created at the film-transparent electrode interface as a result of photon excitation. The existence of the zero-voltage dark current is, however, more difficult



**Fig. 13.** Dark currents and photocurrents (circled symbols) versus temperature ( $10^3/T$ ) for plasma-polymerized thioacetamide (a) and plasma-polymerized pyrazole (b). (\*) 24 V; (x) 6 V; (●) 1.5 V; (▲) 0 V. After Bradley and Hammes.<sup>(4)</sup>

to explain. The data of the zero-voltage, dark conductivity, such as those shown in Fig. 13b, were recorded by Bradley between 30 and 60 min after discontinuing the illumination. Although they appeared to be steady at the time of the measurements, they may have represented long-term residual currents decaying too slowly to be measured over time intervals shorter than days or even perhaps weeks.

The thermal activation energy of photoconduction was the subject of Bradley's second paper.<sup>(51)</sup> This time he followed the photoconduction of plasma polymers prepared from eight monomers over the temperature range  $-77^{\circ}\text{C}$  to  $185^{\circ}\text{C}$  and found some discrete values of activation energies. For instance, plasma-polymerized thiophenol showed activation energy values of 0.054 eV below room temperature and 0.26 eV above it, and the respective values for plasma polymerized pyrrole were 0.052 eV and 0.23 eV.

All of Bradley's results were obtained using the whole spectrum of the tungsten white light source, and no specific dependence on the photon energies was presented. However, if the goal is to approximate the mechanism of photoconduction, the spectral responses of photoconductivity provide a very useful source of information. That is why most researchers following Bradley in this field recorded such dependences.<sup>(10,53-55)</sup> Generally, there are two possible sources of photocurrent carriers, no matter whether these carriers are electrons or holes. One is photoinjection, a surface process in which a number of carriers excited to the level sufficient to overcome the metal-dielectric barrier is injected from the electrode, and the other is photogeneration, a bulk process where carriers are generated inside the dielectric. In the photogeneration process, advantage is usually taken of the existence of additional levels within the forbidden band due to the structural defects or impurities present in the bulk of the dielectric. It is evident, therefore, that the currents controlled by photogeneration should exhibit threshold values of photon energy corresponding to the analogous values of light absorption for the dielectric.

It was Hirai and Nakada<sup>(10)</sup> who first compared these threshold energy values for plasma-polymerized organic films. They investigated plasma-polymerized acrylonitrile samples heat-treated in vacuum. Unfortunately, they did not present results for untreated films, but all their treated samples showed a close correspondence between photocurrent and optical absorption spectra. The threshold energies of photoconduction and the threshold energies of optical absorption extrapolated from these spectra are shown in Table VI for various heat-treatment temperatures. The correspondence of these energies indicate strongly that in the above case photoconductivity is a bulk process.

**Table VI.** Threshold Energies for Plasma-Polymerized Acrylonitrile Films Heat Treated at Various Temperatures<sup>a</sup>

Heat-treatment temperature (°C)	$E_a$ (eV)	$E_c$ (eV)
150	2.22	2.33
200	2.01	2.13
250	1.83	1.91
300	1.68	1.69

<sup>a</sup>  $E_a$  is the threshold energy obtained from optical absorption.  $E_c$  is the threshold energy obtained from photoconductivity. After Hirai and Nakada.<sup>(10)</sup>

Similar conclusions in the case of plasma-polymerized styrene samples sandwiched between gold electrodes have been drawn by Guastavino *et al.*<sup>(53)</sup> They obtained the threshold energy values of optical absorption using two different methods, the reflection technique ( $E_t = 2.06$  eV) and the transmission technique ( $E_t = 2.12$  eV). These values are close enough to the energy threshold value for photocurrent ( $E_t = 2.2$  eV) to support the concept of photogeneration mechanism in this case too. Moreover, the authors postulated that the photogeneration centers occupying an energetic level 2.2 eV below the conduction band in plasma-polymerized styrene contain oxygen which is generally recognized as a systematic impurity in this class of materials. On the other hand, the same plasma-polymerized styrene samples in contact with a cuprous iodide electrode exhibit a surface barrier low enough to make photoinjection the predominant effect in photoconduction, controlling the process to such an extent that the carrier's mobility can be measured based on the sample thickness.<sup>(52)</sup>

The idea of oxygen being responsible for the constitution of the photogeneration centers led Morita *et al.*<sup>(54)</sup> to carry out the measurements of photocurrents in plasma-polymerized styrene in vacuo, without any former contact with the atmosphere. They built the equipment which enabled them to perform all the steps of the experiments, i.e., plasma polymerization, electrode deposition, and photocurrent measurements, in one vacuum run, practically eliminating the influence of atmospheric oxygen. The authors compared the photocurrents of such a fresh sample with the results for the same sample exposed to the atmosphere for 1 h and then evacuated again. Both types of electrode arrangements, i.e., symmetrical (gold/PPS/gold) and asymmetrical (gold/PPS/aluminum) were examined the same way in order not to exclude the possibility of photoinjection. For the symmetrical-electrode experiment, there was significant difference between the results

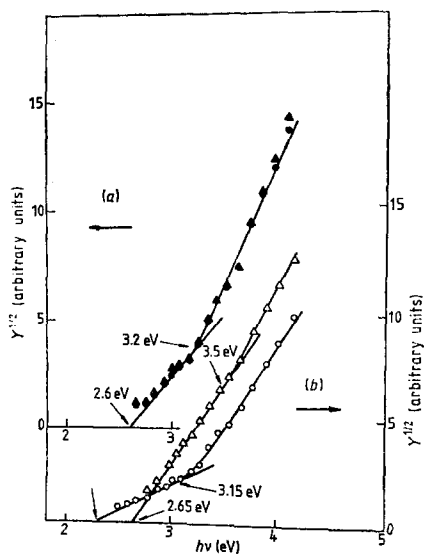
of fresh sample measurements and those after exposure to the atmosphere. The threshold values were  $E_t = 1.6$  eV and  $E_t = 2.1$  eV, respectively, the latter being very close to those obtained by Guastavino.<sup>(52)</sup> Morita seems to attribute the lower threshold value for the oxygen-free sample to the presence of radicals. Being an electron acceptor, the radical would therefore be contributing to the hole generation and following the hole type of conduction; indeed, positive photocurrents were observed in this case. When asymmetrical electrodes were used, however, the situation became more complicated. Air-exposed samples showed the same threshold value for both polarities of the sandwich,  $E_t$  being 2.0 eV. The virgin sample, however, exhibited different threshold values for positive and negative photocurrents ( $E_{t\text{pos}} = 2.6$  eV, whereas  $E_{t\text{neg}} = 1.9$  eV). This finding led the authors to the conclusion that although in most cases photogeneration is very likely responsible, the mechanism in the fresh sample with an asymmetric setup must be of a different nature, depending on the electrode material.

Very recently, a paper has been published by Tyczkowski and Kryszewski<sup>(55)</sup> dealing with the photocurrents in plasma-polymerized organosilicone thin films in which the photoinjection mechanism, rather than photogeneration, is emphasized. They investigated three kinds of materials: plasma-polymerized hexamethyldisilazane, plasma-polymerized hexamethyldisiloxane, and plasma-polymerized hexamethyldisilane and found two different threshold energy values in each case, none of them, however, corresponding to the optical absorption threshold. Again, various electrode combinations were used, i.e., symmetrical Au/Au and Al/Al as well as asymmetrical Au/Al systems. The samples were also measured in two different states, first as fresh ones and then after heat treatment at 350°C for 2 h in an atmosphere of N<sub>2</sub> with 0.5% of O<sub>2</sub>.

Figure 14 presents the experimental threshold values for fresh and heat-treated plasma-polymerized hexamethyldisiloxane with asymmetric electrodes obtained by means of Fowler's diagram, i.e., by plotting the square root of photocurrent quantum efficiency  $Y$  against photon energy  $h\nu$ . The quantity  $Y$  is defined as

$$Y = i_{\text{ph}} / P_c \lambda$$

where  $i_{\text{ph}}$  is the photocurrent,  $P_c$  is the light intensity, and  $\lambda$  is the light wavelength. It is obvious from this figure that the thermally treated sample responds to the electrode material, giving different threshold values for different polarization, hence the conclusion of photoinjection. On the other hand, the fresh sample is not sensitive to the polarization, which rather suggests photogeneration. The authors attribute, however, one general mechanism to all of their specimens, based on the disagreement with the optical absorption as well as on the reproducibility of the double threshold pattern. According to this mechanism, the lower threshold is due to the



**Fig. 14.** Fowler's diagram for plasma-polymerized hexamethyldisiloxane in an asymmetrical electrode system (a) before (filled symbols) and (b) after (open symbols) thermal treatment (2 h). Measurements for two opposite polarizations ( $\circ$ ,  $\bullet$ ) -Al; ( $\triangle$ ,  $\blacktriangle$ ) +Al. After Tyczkowski and Kryszewski.<sup>(55)</sup>

photoinjection of holes from the positive electrode, whereas the higher threshold is due to the photoinjection of electrodes from the negative electrode.

### 3.4. Mechanism of Electrical Conduction

There are generally three basic questions involved in the consideration of electric dc conduction through any material. These questions are: first, what kind of charge carriers are engaged in the conduction process; second, how carriers are produced (or introduced) in the material; and last, but not least, whether the conductivity is governed by charge appearance phenomena or by charge transport. As far as the types of charge carriers are concerned, generally they may be of either electronic or ionic nature, and, more specifically, the electronic species may be electrons or holes and the ionic species may be negative or positive. In the case of conventional polymers, the ionic contribution is usually negligible, and it is not taken into consideration unless the polymer itself is ionic.<sup>(41)</sup> In the case of plasma-polymerized materials, however, there are several indications that ions are present in the polymer and their contribution to the total conduction mechanism cannot be *a priori* neglected. The shift of  $C(V)$  characteristics under the influence of an external, stationary field reported by Maisonneuve for plasma-polymerized styrene (see Section 2.4) has been explained on the basis of positive-ion contribution, for instance.<sup>(34)</sup> Sapielha *et al.*<sup>(56)</sup> have

discovered the phenomenon of charge trapping in plasma-polymerized hexamethyldisiloxane, which may also be attributed to the presence of ionic species. The effect of ionic conductivity may be reduced to a negligible level in the case of plasma polymers also by applying a polarization field for a time long enough for all the ions to reach the respective electrodes and to settle on the contact, which results in stationary currents.<sup>(41)</sup> Nevertheless, one has to remember that, due to the space charge effects, the barrier properties on the electrode-dielectric contact are modified by these ions.

Most researchers studying the conduction mechanism in plasma-polymerized materials consider, however, electronic types of carriers only, trying to answer the remaining two questions. Similar to photoconduction, there are generally two ways in which electronic carriers appear in the dielectric material being considered. One is injection of carriers from the electrode by means of thermal or field-assisted emission, usually referred to as Schottky emission. The other process, where carriers are produced by dissociation of donor-acceptor centers in the bulk of the material, is called Poole-Frenkel generation. If generation processes are slower than carrier transport through the dielectric, the conduction is controlled by generation, specifically either by Schottky or by Poole-Frenkel mechanisms. Conversely, when transport is slower than generation, it constitutes the rate-determining step and the conduction is described by the space-charge-limited-current theory (SCLC).

The common routine widely used by many authors to distinguish between the above mechanisms is to record current dependences on both voltage and sample thickness and to compare these relationships to those predicted by the respective theories.<sup>(40-43,57-60)</sup>

As far as the SCLC theory is concerned,<sup>(57)</sup> it predicts the conduction current density to be proportional to the following:

$$j \sim U^{l+1} / d^{2l+1}$$

where  $l \geq 1$ ,  $U$  is the applied voltage, and  $d$  is the sample thickness. For a given sample thickness, the dependence of  $\ln j$  on  $\ln U$  should thus be linear with slope  $a \geq 2$ , and for a fixed voltage the dependence of  $\ln j$  on  $\ln d$  should also be linear with slope  $b \leq -3$ .

If the generation process, however, is the rate-determining step, the current density (for both Schottky as well as Poole-Frenkel mechanisms) is given by<sup>(56)</sup>

$$\ln j = (\beta/kT) U^{1/2} d^{-1/2} + C$$

where  $k$  is Boltzmann's constant,  $T$  is the temperature,  $C$  is assumed to

be constant, and  $\beta$  is a coefficient characteristic for each of the two mechanisms. This coefficient is expressed as

$$\beta = (e^3 / a\pi\epsilon\epsilon_0)^{1/2}$$

where  $e$  is the elementary charge,  $\epsilon$  is the dielectric constant of the sample,  $\epsilon_0$  is the permittivity of free space, and the coefficient  $a$  is equal to 4 for the Schottky emission mechanism and to 1 for the Poole–Frenkel generation mechanism. Thus

$$\beta_S = \frac{1}{2}(e^3 / \pi\epsilon\epsilon_0)^{1/2}$$

and

$$\beta_{PF} = (e^3 / \pi\epsilon\epsilon_0)^{1/2} = 2\beta_S$$

Generally, therefore, for the conduction process controlled by carrier generation the relationship between  $\ln j$  and  $U^{1/2}$  should be linear, and the value of  $\beta$  calculated from the slope of such a plot should distinguish between Schottky emission and Poole–Frenkel generation. It should be stressed, however, that the difference between  $\beta_S$  and  $\beta_{PF}$  is not critical, which together with the cumulated experimental error often makes such distinction very difficult and sometimes even impossible in the case of polymeric materials. An especially dangerous procedure here is to assume the value of the dielectric constant. It is very easy to show that a change in the assumed value of  $\epsilon$  from 2 to 5 brings about a decrease in the theoretically calculated  $\beta$  coefficients by a factor of 1.581, which is already dangerously close to the number 2 used to distinguish between the two mechanisms. For this reason, any serious study on the nature of the conduction mechanism should be followed by very careful measurements of the dielectric properties, especially dielectric constants. Because of such uncertainty in establishing the conduction mechanism on the basis of  $\beta$  coefficient measurements only, other methods are also used, the most common of which is the application of asymmetric electrodes. The Schottky type of conduction, being based on the emission process, should be sensitive to the properties of the electrode material and especially to the value of its work function. In other words, when Schottky emission is the current-limiting step, the exchange of the field polarity should bring about a shift in the current–voltage characteristic of the asymmetric system by several orders of magnitude (depending on the difference between the work function of the respective electrode materials).

As far as plasma polymers are concerned, most researchers investigating their conduction mechanism recorded the linear relationships of  $\ln j$  versus  $U^{1/2}$  and, based on this evidence, conclude that charge appearance is the rate-limiting step in the conduction. Vollman, for instance, reported such

relationships for plasma-polymerized tetrafluoroethylene,<sup>(40)</sup> Tyczkowski for plasma-polymerized hexamethyldisilazane and hexamethylcyclotrisilazane,<sup>(41-42)</sup> Carchano for plasma-polymerized styrene,<sup>(58)</sup> and Szeto for plasma-polymerized tetramethylsilane.<sup>(43)</sup> The distinction between Schottky and Poole-Frenkel mechanisms, however, does not seem to be that clear in any of the above cases. The experimental arguments used by the authors to distinguish between the two mechanisms as well as the model finally chosen in each case are presented in Table VII. There are several aspects of the above discussion which have to be stressed here. One is the fact that in most cases it is difficult to decide on the mechanism based on a comparison between the  $\beta$  coefficients. Sometimes, as in Refs. 41 and 58, the final choice is actually opposite to the one suggested by the value of  $\beta$ . Moreover, some of the authors used the same magnitude of the dielectric constant  $\epsilon = 3.5$  for different materials and came up with the same values of  $\beta_S = 2.03 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$  and  $\beta_{PF} = 4.06 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$ . It is not, however, quite clear from the published data which researchers measured the dielectric constant and which ones just assumed its value. The other, even more uncertain, point seems to be the experiment with the asymmetric electrodes. Most of the cited authors excluded the possibility of Schottky emission since the change in the sample polarity did not bring about any significant shift in the current-voltage characteristic of the asymmetric system. Tyczkowski,<sup>(42)</sup> on the other hand, who suggests a Schottky mechanism for his samples, records only a slight (but reproducible) difference between the currents for opposite polarities, much smaller than that predicted from the values of the respective work functions. He argues, however, that due to the presence of the surface states, equalization of the metal-dielectric contact barriers can take place in the asymmetric system and bring about its symmetrization. This argument, if confirmed, can weaken significantly the reason for the generally accepted choices of the Poole-Frenkel mechanism in most of the remaining cases since these choices have usually been based on the negative result of the asymmetric-electrode experiment.

All of the authors cited above have excluded the SCLC model of conductivity for their samples based on the nonlinearity of  $\ln j$  versus  $\ln V$  relationships. Nevertheless, Phadke *et al.* have shown space-limited currents for two other systems: plasma-polymerized malononitrile<sup>(59)</sup> and plasma-polymerized ferrocene.<sup>(60)</sup> In the case of plasma-polymerized malononitrile, for instance, Phadke recorded several linear regions in  $\ln j$  versus  $\ln V$  characterized by different coefficients, and he attributed these regions to the different modes of the SCLC mechanism depending on the space-charge interaction with the traps present in the polymer. On the other hand, Tyczkowski<sup>(57)</sup> argues that the linearity of the  $\ln j$  versus  $\ln V$  dependence



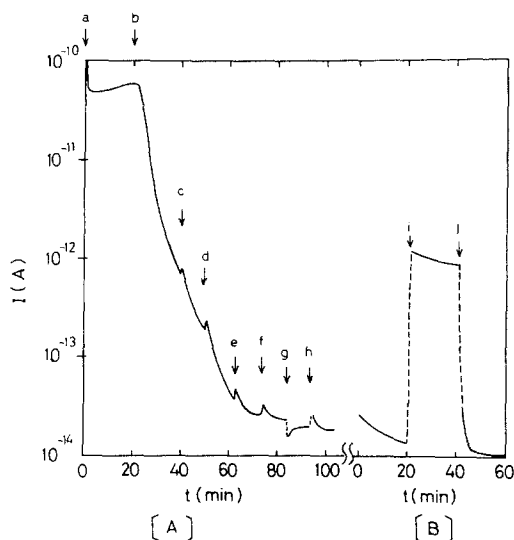
**Table VII.** Experimental Arguments Used in the Literature to Distinguish between Schottky Emission and Poole-Frenkel Generation Processes

Plasma polymerized	$\beta_{\text{theor}} \times 10^5$ (eV m <sup>1/2</sup> V <sup>-1/2</sup> ) $\beta_S$	$\beta_{\text{exp}} \times 10^5$ (eV m <sup>1/2</sup> V <sup>-1/2</sup> ) $\beta_{\text{FP}}$	$\beta_{\text{exp}} \times 10^5$ (eV m <sup>1/2</sup> V <sup>-1/2</sup> )	Asymmetric electrodes experiment	Other experimental arguments used	Suggested mechanism	Reference
Tetrafluoroethylene	2.43	4.86	1.8-6.2	No dependence on polarity		Poole-Frenkel generation modified by impurity centers	Vollman <i>et al.</i> <sup>(40)</sup>
Hexamethyldisilazane	2.03	4.06	1.9-2.7	Negligible dependence on polarity		Poole-Frenkel generation	Kryszewski <i>et al.</i> <sup>(41)</sup>
Hexamethylcyclotrisilazane	2.03	4.06	1.41-2.10	Slight but reproducible dependence on polarity	Lack of field influence on maximum temperature in thermally stimulated current experiment	Schottky emission	Tyczkowski <i>et al.</i> <sup>(42)</sup>
Tetramethylsilane	2.03	4.06	2.3-3.3	No dependence on polarity		Poole-Frenkel generation	Szeto <i>et al.</i> <sup>(43)</sup>
Styrene	2-2.18	4-4.36	2.4	No dependence on polarity	Good agreement between experimental values of activation energies of conductivity and theoretical values for P-F model	Poole-Frenkel generation	Carchano <i>et al.</i> <sup>(58)</sup>

with slope  $n \geq 2$  and the linearity of the  $\ln j$  versus  $\ln d$  dependence with slope  $m \leq -3$  are necessary but not sufficient conditions for determining the presence of space-charge-limited currents. There is, indeed, a great deal of ambiguity and disagreement in the whole discussion on conduction mechanism and, in some cases, the authors change even their own viewpoints in more recent publications.

There is one more aspect of the conduction phenomenon in plasma-polymerized thin films which has to be discussed, and this is the instability of the mechanism after exposure to the atmosphere. Not all of the authors cited above specified exactly whether their samples had been exposed to the atmosphere prior to the measurements, but Szeto, for instance, reported a significant difference between exposed and unexposed samples. The data shown in Table VII concern fresh a sample, which in an asymmetric electrode setup did not exhibit any current dependence on polarity. This sample, however, when exposed to humid air, loses its current symmetry with respect to polarity, indicating significant differences in the conduction mechanism, presumably switching from Poole-Frenkel generation to Schottky emission models. Szeto does not point out which particular component of the atmosphere is responsible for the observed effect. It has been shown elsewhere, however, that there are two factors which are of great importance: oxygen and humidity.<sup>(21,59,61)</sup> As far as the magnitude of dark conductivity is concerned, oxygen decreases this value<sup>(21,59)</sup> and humidity increases it.<sup>(21,61)</sup> Perhaps the best illustration of this relationship has been given by Morita<sup>(21)</sup> for plasma-polymerized styrene (Fig. 15). This figure illustrates the sample current changes brought about by its exposure to dry oxygen and reevacuation (A) as well as its exposure to humid air (74% R.H. at 28°C) and its reevacuation (B). The letters on the curve indicate the following experimental steps: (a) application of a voltage of 1 V on the virgin sample in vacuum; (b)–(e) introduction of oxygen to 0.1, 1, 10, and 20 Torr, respectively; (f) reevacuation; (g) reintroduction of oxygen to 20 Torr; (h) reevacuation; (i) introduction of humid air to 1 atm; (j) reevacuation. As is seen in Fig. 15, introduction of oxygen brings about a decrease in conductivity by more than three orders of magnitude, and this effect is irreversible [see step (f)]. The introduction of water vapor, on the other hand, causes an increase in conductivity, which is reversible [see step (j)]. It should be stressed here that an analogous experiment with the introduction of pure argon to 10 Torr and 1 atm showed no significant changes in current within the same period of time (80 min).

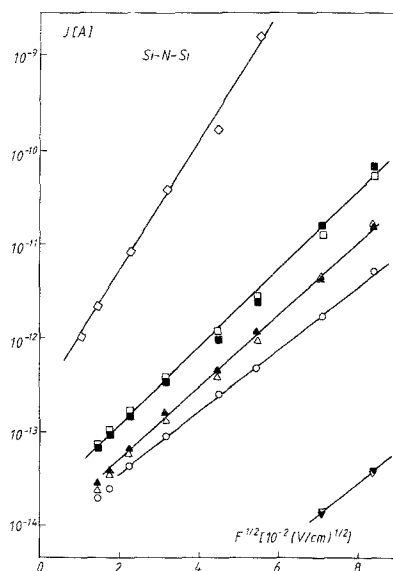
Knowing that oxygen and humidity influence mainly the instability of the electrical conduction of plasma polymers, it appears obvious that the best method of controlling such instability is first to understand the mechanism of these influences. A recent work of Tyczkowski<sup>(61)</sup> dealing exclusively



**Fig. 15.** Changes of conduction current of a plasma-polymerized styrene sample exposed to dry oxygen (A) and humid air (B). After Morita *et al.*<sup>(21)</sup>

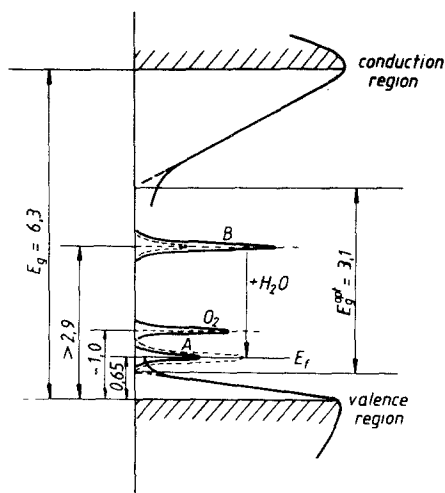
with the conduction in plasma-polymerized films in the presence of water and oxygen is an attempt to explain this mechanism. The author investigated plasma-polymerized organosilicone films and observed an increase in conductivity in both cases, i.e., under the influence of water as well as oxygen. As far as conduction in the presence of water is concerned, there are suggestions in the literature that this may be due to an ionic contribution to the total mechanism resulting from the dissociation of water.<sup>(61)</sup> In order to confirm or to reject this hypothesis, Tyczkowski performed his measurement twice: once in the presence of water vapor and once in the presence of heavy water vapor. Heavy water has an ionic product 5.2 times smaller than water and the mobilities of  $D^+$  and  $OD^-$  ions are 1.4 and 1.66 times smaller than the mobilities of  $H^+$  and  $OH^-$  ions, respectively. All of the above data indicate that if ionic species were really the charge carriers in this case, the currents should be lower for the  $D_2O$  experiment. Figure 16 presents the results of this experiment. The lack of a difference between the influence of water and heavy water strongly suggests the electronic character of the conduction. On the other hand, Tyczkowski has shown that the concentration of acceptor centers increases substantially with increasing relative humidity. The author claims, however, that water itself does not constitute these centers, but rather activates primarily inactive centers already present in the polymer structure. A thermally treated polymer, for instance, is no longer susceptible to the influence of water,

**Fig. 16.** Dependence of current on square root of field for plasma-polymerized hexamethyldisilazane, as-polymerized ( $\circ, \triangle, \square, \diamond$ ) and thermally treated ( $\nabla$ ). Measurements in different humidity conditions: as polymerized samples,  $\circ$ —in dry nitrogen;  $\triangle$ —RH = 8%;  $\blacktriangle$ —RH(D<sub>2</sub>O) = 8%;  $\square$ —RH = 36.5%;  $\blacksquare$ —RH(D<sub>2</sub>O) = 36.5%;  $\diamond$ —RH = 100%; thermally treated samples:  $\nabla$ —in dry nitrogen;  $\blacktriangledown$ —RH = 36.5%. After Tyczkowski *et al.*<sup>(61)</sup>



which suggests that there inactive centers have been removed during the treatment.

As a result of his work, Tyczkowski proposes a simplified band model of his plasma-polymerized organosilicone samples which is assumed to be valid for both siloxane as well as silazane types of structures. This model is presented in Fig. 17. It can be seen in this figure that oxygen constitutes another, additional acceptor center level and, therefore, contributes to the



**Fig. 17.** Scheme of energy level structure of plasma-polymerized organosilicone thin film considering the influence of H<sub>2</sub>O and O<sub>2</sub> absorbed molecules on their conductivity. (A) Intrinsic acceptors responsible for electrical conductivity in the absence of water and oxygen; (B) inactive acceptors which can be activated by water molecules; (O<sub>2</sub>) oxygen acceptors. Values of energy in electron volts. After Tyczkowski *et al.*<sup>(61)</sup>

increase in conductivity. This case seems to be specific for plasma-polymerized organosilicones. As has been shown in the case of other plasma polymers such as plasma-polymerized malononitrile<sup>(59)</sup> or plasma-polymerized styrene,<sup>(21)</sup> a significant decrease in conductivity is observed in the presence of oxygen. Oxygen is well known as a free radical scavenger and that is why these results are consistent with those obtained by Nakamura *et al.*<sup>(62)</sup> who followed the relationships between the conductivity and the concentration of free radicals and found them to be proportional. If free radicals constitute the level lowering the width of the forbidden band, oxygen deactivates this level, and the conductivity of the system should drop.

#### 4. CONCLUSIONS

The literature on the electrical properties of plasma polymers is not very easy to review, just as it is difficult and complex to work in this field. Its complexity originates mainly from the complexity of the material itself; although the material is very often called polymeric, as far as its structure is concerned it has very little to do with polymers in their conventional sense. From the viewpoint of its structure, plasma-polymerized styrene has much more in common with plasma-polymerized toluene or benzene (materials which do not even have conventional correspondents) than with conventional polystyrene. That is why deducing the structural and mechanistic parameters of a plasma polymer based on a comparison with the conventional polymer obtained from the same monomer may often be very misleading. Moreover, the properties of plasma-polymerized materials should be defined in a different way from the properties of the corresponding conventional systems. The properties of the conventional polymers are more or less characteristic for a given material and although they can vary with parameters such as molecular mass or degree of cross-linking, these variations are not too large and the polymer is still recognized by its characteristics. In contrast, the structure and properties of plasma polymers are not well defined and very strongly depend on the energy input used in the deposition process. The average energy input per unit of monomer mass can be conveniently expressed by the  $W/FM$  parameter, where  $W$  is the power input used during deposition,  $M$  is the molecular weight of the monomer, and  $F$  is its feed-in flow rate<sup>(12)</sup>; the polymer properties depend substantially on this parameter. At the same time, however, local energy differences always exist, which are due to the geometry of the particular system, and these differences can bring about significant changes in the polymer properties as well. The best example of such a situation is the case of plasma-polymerized tetramethyltin,<sup>(44,45)</sup> where samples prepared in the same run varied in conductivities by several orders of magnitude depending

on their position along the axis of the tubular reactor. The same example shows how inadequately defined the term "electrical properties of plasma polymers" can be. There is not much sense in discussing the "conductivity of plasma-polymerized tetramethyltin" unless it is precisely specified how this particular material has been prepared.

The next, very significant factor, which makes plasma polymers behave very different when compared to conventional polymeric materials, is the thickness factor. One should note that, when dealing with plasma polymers, thin films of thicknesses between several hundred angstroms to several micrometers are involved. It is quite obvious that in this range of thicknesses the surface effects, being already competitive with the bulk phenomena, also have to be taken into consideration. In particular, some electrical parameters of thin films, such as dielectric strength, conductivity, or even dielectric constant, should depend on their thickness. Out of the thickness aspect another difficulty arises, and this is of rather practical nature. The electrical measurement becomes a problem itself because of the very small thickness of the material. The experimental setup and the material of the electrodes as well as their surface area are sometimes crucial in the whole measurement. Many plasma-polymerized films, for instance, contain weak spots which make the measurements impossible in higher fields, unless the self-healing breakdown procedure is applied. As a matter of fact, based on our personal experience, we would expect that most of the cited literature data were obtained after applying such self-healing procedures, although authors do not usually specify such treatment. On the other hand, by applying a mercury drop electrode of a very small surface area and moving it around the sample, one can eliminate such weak spots naturally if their concentration is not too high.<sup>(14)</sup>

Another general finding concerning the electrical properties of plasma polymers is directly connected with the instability of these materials, a feature that has made it difficult to develop the technology of their applications. It has been shown without doubt that these polymers are very sensitive to the influence of the two major atmospheric substances, i.e., oxygen and humidity. Once adsorbed or bonded to the polymer, these substances may drastically change the values of dielectric losses and conductivities, and even the total conduction mechanism may be switched after the polymer is exposed to the atmosphere. Most researchers are aware of these influences, and significant effort is being made to eliminate them. The best way to do so, we suppose, is to understand the mechanisms of these influences and the structural reasons for the instabilities. More and more authors have begun to recognize such a necessity, and papers have appeared recently dealing specifically with the electrical properties of plasma-polymerized materials under the influence of water and oxygen. There are several general

conclusions which can be drawn from the presently available data concerning the influence of these two substances. The influence of oxygen has been widely reported as an irreversible one, and it is generally attributed to some kind of chemical reaction with the structural groups present in a plasma polymer. The usual interpretations consider either unsaturated bonds or trapped radicals as such groups. Since the structure of plasma polymers is generally still unknown, these reactions can only be hypothetical.

The interaction of water with the structure of a plasma polymer and consequently its influence on the electrical properties is an even more difficult problem. Most papers, for instance, stress that the influence of water is reversible, but there are also examples of its irreversible behavior.<sup>(17)</sup> Most authors agree, however, that water does not create chemical bonding with the structure of a plasma polymer. At least a part of the problem should be attributed, perhaps, to our difficulties in understanding water itself, its structure and behavior, especially from the point of view of surface chemistry.

The general lack of structural information for plasma polymers is a factor which appears very often in the discussion. Building band models such as the one presented in Fig. 17, although very helpful from the energetic point of view, does not improve our structural understanding of plasma polymers, which is still poor. It would truly be a big step forward if we were able to attribute the particular acceptor centers to certain chemical groups present in the structure of the polymer. This seems to be a very difficult goal especially when we remember that, compared to materials used in microelectronics which mostly have a well-defined, crystalline structure with few defects, plasma polymers are amorphous, poorly defined substances having nothing but defects in their structure.

In this attempt to summarize the subject, we should point out the following. Although plasma polymers are a total disappointment to researchers who hope to make a quick and brilliant career in the microelectronics industry, it does not mean that these materials are useless. Plasma polymers are simply much harder to handle, but their primary advantage, i.e., the possibility of controlling their thickness down to about 100 Å, is still unbeatable, and that is why a great deal of research is going on in an attempt to understand the electrical properties of these materials. The more we understand these properties, the better we can control them, which in our opinion is the way to the technological future of plasma polymers.

## ACKNOWLEDGMENTS

This work was supported in part by Contracts NO1-NS-8-2393 and NO1-NS-1-2382 from the National Institute of Neurological and Communicative Disorders and Stroke, NIH, Bethesda, Maryland.

We would also like to thank Dr. Marek Zieliński from New York University for the words of encouragement and stimulating discussions during the writing of this review as well as for the critical reading of the manuscript.

## REFERENCES

1. A. Bradley, Organic Polymer Coating Deposited from a Gas Discharge, *Ind. Eng. Chem. Prod. Res. Dev.* **9**, 101–104 (1970).
2. J. Goodman, The Formation of Thin Polymer Films in the Gas Discharge, *J. Polym. Sci.* **44**, 551–552 (1960).
3. A. Bradley and J. P. Hammes, Electrical Properties of Thin Organic Films, *J. Electrochem. Soc.* **110**, 15–22 (1963).
4. A. Bradley and J. P. Hammes, Photoconductivity in Thin Organic Films, *J. Electrochem. Soc.* **110**, 543–548 (1963).
5. M. Stuart, Dielectric Properties of Crosslinked Polystyrene Film Formed in the Glow Discharge, *Nature* **199**, 59–60 (1963).
6. M. Stuart, Dielectric Losses in Polymer Films Formed by a Discharge, *Proc. Inst. Electr. Eng.* **112**, 1614–1616 (1965).
7. P. J. Ozawa, Organic Thin Film Capacitor, *IEEE Trans. Parts, Mater. Packag.* **PMP-5**, 112–116 (1969).
8. N. M. Bashara and C. T. Doty, Electrical Conduction in Very Thin Polybutadiene Films Formed in a Glow Discharge, *J. Appl. Phys.* **35**, 3498–3507 (1964).
9. L. V. Gregor, Electrical Conductivity of Polydivinylbenzene Films, *Thin Solid Films* **2**, 235–246 (1968).
10. T. Hirai and O. Nakada, Formation of Thin Polyacrylonitrile Films and Their Electrical Properties, *Jpn. J. Appl. Phys.* **7**, 112–121 (1968).
11. A. M. Mearns, Insulator Thin Films Formed by Glow Discharge and Radiation Techniques, *Thin Solid Films* **3**, 201–228 (1969).
12. H. Yasuda, Glow Discharge Polymerization, *J. Polym. Sci., Macromol. Rev.* **16**, 199–293 (1981).
13. Y. Segui and Bui Ai, Microelectronic Applications of Plasma-Polymerized Films, *Thin Solid Films* **50**, 321–324 (1978).
14. E. J. Charlson, E. M. Charlson, A. K. Sharma, and H. K. Yasuda, Electrical Properties of Glow Discharge Polymerized Films, paper presented at the ACS Meeting on Plasma Polymerization and Plasma Treatment, Kansas City, Missouri, September 1982.
15. J. S. Sandved and K. Kristiansen, Glow Discharge Polymerization of Organic Silicones, *Vacuum* **27**, 235–239 (1977).
16. S. D. Phadke, Dielectric Properties of Plasma-Polymerized Ferrocene Films, *Thin Solid Films* **48**, 319–324 (1978).
17. G. Sawa, O. Ito, S. Morita, and M. Ieda, Dielectric Properties of Polystyrene Formed in a Glow Discharge, *J. Polym. Sci., Polym. Phys. Ed.* **12**, 1231–1234 (1974).
18. J. M. Tibbitt, A. T. Bell, and M. Shen, Dielectric Relaxations in Plasma-Polymerized Hydrocarbons and Fluorocarbons, *J. Macromol. Sci. (Part A) Chem.* **10**, 519–533 (1976).
19. U. Hetzler and E. Kay, Conduction Mechanism in Plasma-Polymerized Tetrafluorethylene Films, *J. Appl. Phys.* **49**, 5617–5623 (1978).
20. S. Takeda, Dielectric Properties of Polystyrene Thin Films Formed by RF Electrodeless Excitation, *J. Appl. Phys.* **47**, 5480–5481 (1976).
21. S. Morita, G. Sawa, and M. Ieda, Influence of Oxygen on Electrical Properties of Styrene Thin Films Polymerized in a Glow Discharge, *J. Appl. Phys.* **44**, 2435–2436 (1973).



22. D. Ristow, Time-Dependent Properties of Organic Thin Films Deposited by Glow Discharge, *J. Mater. Sci.* **12**, 1411–1415 (1977).
23. L. S. Tuzov, V. M. Kolotyrkin, and N. N. Tunitskii, Stability of the Dielectric Properties of Polymer Films Formed in a Glow Discharge, *Int. Chem. Eng.* **11**, 60–64 (1971).
24. G. Sawa, S. Yamanaka, S. Nakamura, and S. Yamaguchi, Improvement of Dielectric Properties of Plasma-Polymerized Styrene with Hydrogen Plasma Treatment, *Jpn. J. Appl. Phys.* **20**, L201–L204 (1981).
25. C. Sar, M. Valentin, and Bui Ai, Methods for Lowering Loss Angle Tangent of Thin Polystyrene Films Obtained by Electrical Discharge in Styrene Vapor, *J. Appl. Polym. Sci.* **24**, 503–510 (1979).
26. S. Morita, G. Sawa, and M. Ieda, Thin Polymer Films by the Glow Discharge Indirect Method, *J. Macromolec. Sci. (Part A) Chem.* **10**, 501–517 (1976).
27. C. F. Pratt, M. Gazicki, and H. K. Yasuda, Plasma Polymerization in Magnetically Enhanced audiofrequency Discharge: Dielectric Properties of Films Obtained in Low W/FM Conditions, to be published.
28. M. Hudis and T. Wydeven, Plasma Polymerization of an Ethylene–Nitrogen Gas Mixture, *J. Polym. Sci., Polym. Lett. Ed.* **13**, 549–557 (1975).
29. D. Brosset, Bu Ai, and Y. Segui, New Method of GaAs Passivation with Thin Polymer Films, *Appl. Phys. Lett.* **33**, 87–89 (1978).
30. A. Bui, H. Carchano, and D. Sanchez, Properties of Polymer Thin Films on Silicon, *Thin Solid Films* **13**, 207–211 (1972).
31. D. Sanchez, M. Carchano, and A. Bui, Electrical Properties of Metal–Polymer (Polystyrene)–Silicon Devices, *J. Appl. Phys.* **45**, 1233–1238 (1974).
32. M. Maisonneuve, Y. Segui, and A. Bui, Electrical Properties of Metal–Polymer (Polysiloxane)–Silicon Structures and Application of Polysiloxane to the Passivation of Semiconductor Devices, *Thin Solid Films* **33**, 35–41 (1976).
33. H. R. Anderson, Jr., F. M. Fowkes, and F. H. Hielscher, Electron Donor–Acceptor Properties of Thin Polymer Films on Silicon. II. Tetrafluoroethylene Polymerized by RF Glow Discharge Techniques, *J. Polym. Sci., Polym. Phys. Ed.* **14**, 879–895 (1976).
34. M. Maisonneuve, Y. Segui, and A. Bui, Charge Transport in Thin Polymer Films as Shown by C–V Measurements, *Thin Solid Films* **44**, 209–216 (1977).
35. R. Szeto and D. W. Hess, Correlation of Chemical and Electrical Properties of Plasma-Deposited Tetramethylsilane Films, *J. Appl. Phys.* **52**, 903–908 (1981).
36. H. Pachonik and G. Seebacher, Eigenschaften Dunner Glimmpolymerisierter Schichten, *Thin Solid Films* **38**, 343–352 (1976).
37. S. Sapieha, W. Jablonski, and M. Kryszewski, The Structure of Incomplete Destructive Breakdown Spots in Thin Polymer Films, *Electrocomponent Sci. Technol.* **1**, 65–73 (1974).
38. S. Sapieha and M. Kryszewski, Elektryczna i optyczna stymulacja przebieg w cienkich warstwach dielektryków, *Arch. Elektrotech. (Warsaw)* **23**, 739–748 (1974).
39. S. Sapieha, M. R. Wertheimer, and A. Yelon, A Simple Method for Breakdown Voltage Measurements in Thin Films, *IEEE Trans. Electr. Insul.* **EI-14**, 229–230 (1979).
40. W. Vollman and H.-U. Poll, Electrical Conduction in Thin Polymer Fluorocarbon Films, *Thin Solid Films* **26**, 201–211 (1975).
41. M. Kryszewski, A. M. Wróbel, and J. Tyczkowski, Plasma-Polymerized Organosilicon Thin Films—Structure and Properties, in: Plasma Polymerization, M. Shen and A. T. Bell, eds., *Am. Chem. Soc. Symp. Ser.* **108**, 219–236 (1979).
42. J. Tyczkowski, M. Zielinski, and M. Kryszewski, On the Mechanism of Electrical Conduction in Glow Discharge Polysilazane Films, *Thin Solid Films* **55**, 253–259 (1978).
43. R. Szeto and D. W. Hess, Conduction Mechanism in Plasma-Polymerized Tetramethylsilane Films, *Thin Solid Films* **78**, 125–132 (1981).

44. E. Kny, L. L. Levenson, W. J. James, and R. A. Auerbach, Organotin Polymers Formed by Glow Discharge Polymerization, *J. Phys. Chem.* **84**, 1635–38 (1980).
45. E. Kny, L. L. Levenson, W. J. James, and R. A. Auerbach, Formation and Properties of Metallic Organotin Films, *Thin Solid Films* **85**, 23–32 (1981).
46. R. K. Sathir, W. J. James, and R. A. Auerbach, Preparation and Properties of Metallic Organotin Films by Glow Discharge Polymerization, *Thin Solid Films* **97**, 17–29 (1982).
47. R. K. Sathir, W. J. James, and R. A. Auerbach, Synthesis and Properties of Thin Film Organotin Polymers by Glow Discharge Polymerization, private communication to be submitted.
48. R. K. Sathir, W. J. James, and R. A. Auerbach, Synthesis of Organogermanium Films by Glow Discharge Polymerization, paper presented at the ACS Meeting on Plasma Polymerization and Plasma Treatment, Kansas City, Missouri, September 1982.
49. H. Carchano, R. Lacoste, and Y. Segui, Bistable Electrical Switching in Polymer Thin Films, *Appl. Phys. Lett.* **19**, 414–415 (1971).
50. Y. Segui, Bui Ai, and H. Carchano, Switching in Polystyrene Films: Transition from On to Off State, *J. Appl. Phys.* **47**, 140–143 (1976).
51. A. Bradley, Photoconduction in Thin Organic Polymer Films, *Trans. Faraday Soc.* **61**, 773–780 (1965).
52. J. Guastavino, H. Carchano, and Ai Bui, Mesure de la mobilité de charges positives injectées par une électrode de CuI dans une couche mince de polymère, *Thin Solid Films* **24**, S23–S26 (1974).
53. J. Guastavino, H. Carchano, and Ai Bui, Photoconductivité de couches minces de polymère obtenues par décharge électrique dans de vapeurs de styrene, *Thin Solid Films* **27**, 225–238 (1975).
54. S. Morita, M. Shen, and M. Ieda, *In vacuo* Photocurrent Measurements of Plasma-Polymerized Styrene Films, *J. Polym. Sci., Polym. Phys. Ed.* **15**, 981–986 (1977).
55. J. Tyczkowski and M. Kryszewski, Photoinjection into Plasma-Polymerized Organosilicon Thin Films: I. Surface States, *J. Phys. D: Appl. Phys.* **14**, 1877–1888 (1981).
56. J. E. Klemberg-Sapieha, S. Sapieha, M. R. Wertheimer, and A. Yelon, Charge Trapping in Plasma-Polymerized Thin Films, *Appl. Phys. Lett.* **37**, 104–105 (1980).
57. J. Tyczkowski, G. Czeremuszkin, and M. Kryszewski, On Differentiation of Electrical Conduction Processes in Polymers, *Phys. Status Solidi (A)* **72**, 751–762 (1982).
58. H. Carchano and M. Valentin, Étude électrique de couches minces de polymère obtenues dans une décharge luminescente: I. Caractérisation électrique sous champ continu, *Thin Solid Films* **30**, 335–349 (1975).
59. S. D. Phadke, Space-Charge-Limited Currents and Carrier Trapping in Plasma-Polymerized Malononitrile Films, *Thin Solid Films* **55**, 391–397 (1978).
60. S. D. Phadke, K. Sathianandan, and R. N. Karekar, Electrical Conduction in Polyferrocene Thin Films, *Thin Solid Films* **51**, L9–L11 (1978).
61. J. Tyczkowski and M. Kryszewski, Electrical Conduction in Plasma-Polymerized Organosilicone Films: Influence of Water and Oxygen, paper presented at the ACS Meeting on Plasma Polymerization and Plasma Treatment, Kansas City, Missouri, September 1982.
62. S. Nakamura, S. Yamanaka, S. Yamaguchi, and G. Sawa, The Correlation of Transient Electric Current with Free Radicals in Plasma-Polymerized Styrene, *Jpn. J. Appl. Phys.* **19**, 767–768 (1980).