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## Thin Polymer Films by the Glow-Discharge Indirect Method

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### A B S T R A C T

The growing mechanism and the structure of thin polystyrene film by the glow discharge-indirect method are discussed. A theoretical relationship between the growth rate of polymerized film and the discharge condition is deduced on the basis of Poll's model, taking the charge transport processes in the discharge space into consideration: 1) the ambipolar diffusion, 2) the recombination of charges forming the ion sheath, and 3) the effect of stray capacity. Substitution of possible values of physical parameters on the gaseous plasma into the theoretical relation give a reasonable growth rate which agrees well with the experimental results. From NMR, ESR, and dielectric experiments, it is suggested from the molecular and morphological structure of the film that small molecules and free radicals remain, but most of the film consists of a three-dimensional mesh structure.

## INTRODUCTION

Thin polymer films have been given much attention from a practical point of view in microelectronics as well as there being an interest in their electrical properties at high electric fields and their surface phenomena [1-5]. Various methods have been proposed for the preparation of thin polymer films such as glow discharge, electron bombardment, photolysis, and evaporation. Among them, glow-discharge polymerization is widely used since thin films prepared by this method are pinhole-free and have excellent electrical, mechanical, and chemical properties [6].

The usual procedure for producing a polymer film by the glow-discharge method (GD film) is as follows [7]. A couple of electrodes are set in a glass chamber filled with organic monomer vapor, and an ac glow discharge is initiated between the electrodes. Thin polymer films are then polymerized on the discharge electrodes or on the substrates set in the plasma. Methods thus far proposed for the polymerization in the glow discharge are listed in Table 1 [8-25]. The method in which the film is polymerized on the substrate set in the discharge space is sometimes called the indirect method, while the method in which the film is deposited directly on the surface of the discharge electrode is called the direct method.

Much work has also been done on electrical properties of the GD film such as electrical conductions [26-30], dielectric properties [9, 31-34], and dielectric breakdown [35-37]. It has been shown that the electrical properties of the GD film are different from those of conventional polymers. Both the dielectric loss factor  $\tan \delta$  and the conductivity are usually larger than those of conventional polymers. The molecular structure and morphology of the film are also different from conventional polymers. The heat resistance of the GD film is usually higher than that of conventional polymers. Most GD films do not melt at temperatures much higher than the melting point of the corresponding conventional polymers. Therefore, the GD film seems to be highly cross-linked [38]. In addition, free radicals [18, 23, 39] and molecules of low molecular weight [11] occasionally remain in the films. The former would react with oxygen in air [40], and the latter would be released from the film by heat treatment. The molecular and morphological structures would be sensitive to polymerization conditions in the glow discharge.

In this paper, following a brief review of the growing mechanisms so far reported, a model is presented for film growth by the glow-discharge indirect method and is compared with experimental results. The essential feature of this model is to include the basic concepts of gaseous glow discharges. In addition, the molecular and morphological structures are discussed, based on the experimental results of the NMR, ESR, and dielectric properties.

TABLE 1. Methods Proposed for the Polymerization in the Glow Discharge

Types of discharge	Position of substrate	Reference
dc glow	On electrode	König et al. [8]
	On the third electrode	Ando et al. [9]
Commercial frequency glow	On electrode	Hirai [10]
	In plasma	Paciorek et al. [11]
Low-frequency glow	On electrode	Bradley et al. [12]
		Williams et al. [13]
		Poll [14]
	Abe et al. [15]	
In plasma	Ozawa [16]	
	Morita et al. [17]	
High-frequency glow (higher than a few MHz)	On electrode	Denaro et al. [18]
		Westwood [19]
		Brown [20]
		Kobayashi et al. [21]
Electrodeless glow	In plasma	Connel [22]
		Millard et al. [23]
	In the flow of gas	Lee [24]
		Yasuda et al. [25]

## EXPERIMENTAL

A schematic diagram of the apparatus for growing the polymer film by the glow-discharge indirect method is shown in Fig. 1. Styrene vapor was used as the monomer gas, which was distilled by the usual procedure [34]. A typical example of polymerization condition included a gas pressure of about 0.5 Torr, a frequency of the applied voltage of a few kHz, a current density of discharge of a few mA/cm<sup>2</sup>, and a discharge duration of a few minutes. A GD polystyrene film of a few thousand angstroms in thickness was deposited under the above discharge condition.

Experiments for studying the growth rate of GD polymer was performed in the following way. The film thickness was

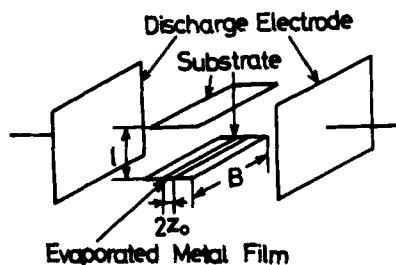


FIG. 1. Diagram of discharge polymerization system.

obtained as a function of one of the parameters of the discharge conditions with all the other parameters kept constant. The parameters considered were discharge current, gas pressure, time of discharge duration, and discharge frequency. The film thickness was estimated from the capacitance, assuming a value of 2.6 for the dielectric constant.

The NMR measurement was made on a solution of the polymer samples in benzene-d<sub>6</sub> and 1% TMS at room temperature. For the ESR measurement, the films polymerized on a mica foil were used and two kinds of samples were prepared. Sample I was kept in air and sample II was kept in a vacuum of  $\sim 10^{-3}$  Torr. The ESR measurements were performed at room temperature by using an x-band spectrometer with a field modulation of 100 kHz.

### GROWING MECHANISM [17]

The growth of the thin film by the glow-discharge indirect method can be divided into three processes: the activation of monomer species by the glow discharge, the transport of activated particles, and the polymerization. These processes depend on the kind of monomer, the discharge configuration, and the discharge condition. These factors determine whether the polymerization occurs in the gas phase or on the substrate. In ordinary conditions the radical reaction in the gas phase has been considered to be predominant in polymerization at a discharge frequency higher than a few MHz [18, 21], but the reaction on the substrate by ions predominates at lower discharge frequency [13, 14, 17]. In the latter case the transport process of ions is thought to be most important in determining the growth rate of the polymer film.

In the following section the transport process of ions is discussed in detail.

Poll's Theory [14]

The number of monomer units in the polymerized film per unit time and unit area is given by

$$P = \frac{\gamma\Phi}{1 + \frac{\gamma\Phi}{gn_{\infty}R}} \approx gn_{\infty}R \quad (1)$$

for  $gn_{\infty}R \ll \gamma\Phi$ , which is usually satisfied. In Eq. (1),  $\Phi$  is the number of monomer molecule coming onto the substrate per unit area and unit time,  $\gamma$  is the adherent coefficient,  $R$  is the number of particles which contribute to polymerization per unit area and unit time, and  $g$  is the effective cross-section of molecule. Taking  $\tau$  as the mean adsorbed time of a molecule,  $1/n_{\infty} = 1/n_0 + 1/\gamma\Phi\tau$  is obtained, where  $n_0$  is the number of monomer per unit area in a monolayer. The growth rate  $W$  of film is given as

$$W = \frac{M}{L\rho} P \approx \frac{M}{L\rho} gn_{\infty}R \equiv KR \quad (2)$$

where  $K$  is defined as  $K = Mgn_{\infty}/L\rho$ ,  $M$  is the molecular weight of monomer,  $L$  is Avogadro's number, and  $\rho$  is the density of the polymerized film. The value  $gn_{\infty}$  indicates the number of monomer units polymerized by an incident ion.

Poll has shown good agreement between the above equation and experimental results for the film polymerized from tetrafluoroethylene monomer vapors by a 50-KHz glow-discharge direct method. He has obtained values of 3 to 4 for  $gn_{\infty}$  except in the case of 0.1 Torr as shown in Table 2. Abe et al. [15] have also reported that about 3.5 monomer units are polymerized by an ion with the glow-discharge direct method in styrene vapor at 1.0 Torr and 6 kHz.

Growing Mechanism in the Glow-Discharge Indirect Method [17]

When the predominant reaction is induced by charged particles, the growth rate of the film can be estimated based on Poll's model

TABLE 2. Experimental Values of  $gn_{\infty}$  for the Film Polymerized from Tetrafluoroethylene Monomer Vapors by a 50-kHz Glow Discharge [14]

P (Torr)	0.1	0.25	0.35	0.5	0.75	1.5
$gn_{\infty}$	1.06	3.68	3.94	3.92	3.54	3.12

if a value of  $R$  in Eq. (2) is evaluated. In the glow-discharge direct method, the value  $R$  can be easily estimated, but in the indirect method, there has been no attempt to estimate it. Here a model is presented where the basic concepts for the gaseous glow discharge are involved.  $R$  is determined by the transport processes of charged particles onto the substrate for which the following three mechanisms can be considered.

The first is ambipolar diffusion. Just after the discharge starts, electrons diffuse to the substrate and then an ion sheath is formed around it. The stationary state is established when the same number of electrons and ions are diffused to the substrate by ambipolar diffusion. The sequence is repeated at every half cycle. The number of ions flowing onto the substrate per unit time in the stationary state can be calculated from the ambipolar diffusion process in the positive column. The growth rate due to the ambipolar diffusion ( $W_a$ ) is expressed in the case of the electrode system of Fig. 1 as

$$W_a = K \frac{2.7kT}{qB\ell^2\delta^2\sqrt{\kappa}} \frac{\mu_i}{\mu_e} \frac{I}{p} \quad (3)$$

where  $k$  is Boltzmann's constant,  $T$  is the gas temperature,  $\mu_i$  and  $\mu_e$  are the mobilities of ion and electron, respectively,  $q$  is the electronic charge,  $\delta$  is the diameter of monomer,  $\kappa$  is the width in the cross-section of the discharge path,  $\ell$  is the gap length between the substrates,  $I$  is the discharge current, and  $p$  is the gas pressure.

Second, we must take into account the initial diffusing charges when the discharge frequency increases. In the case of alternating current, the number of positive ions in the ion sheath varies with time within a half cycle, and positive ions in the ion sheath can recombine with the adsorbed electrons on the surface at each half cycle, leading to an increase in the number of positive ions

reaching the surface. The growth rate due to the recombination of charges forming the ion sheath ( $W_f$ ) is expressed as,

$$W_f = 4K \left\{ \frac{\left\{ \ln \left( \frac{T_e m_i}{T_i m_e} \right) \right\}^{1/2} - 2}{\ln \frac{T_e m_i}{T_i m_e}} \right\} \frac{\lambda_s f}{\sqrt{e}} N_0 \tag{4}$$

where  $T_i$  and  $T_e$  are the temperatures of the ions and electrons, and  $m_i$  and  $m_e$  the masses of the ions and electrons, respectively,  $\lambda_s$  is the thickness of the ion sheath,  $f$  is the frequency of the applied voltage,  $e$  is the base for natural logarithms, and  $N_0$  is the charge density in the plasma region.

Strictly speaking, the two components described above are not independent of each other within a half cycle, but for the sake of simplicity the two processes will be treated separately.

Lastly, the influence of evaporated metal on the substrate is considered. When the metal film is evaporated on the substrate, the potential at any point on the evaporated metal film is constant. In contrast to this, the potential in the discharge space over the metal film varies from point to point along the discharge axis, yielding the potential difference between the metal on the substrate and the discharge space. Due to these potential differences, a part of the main discharge current will flow into the metal film as shown in Fig. 2.

Then the resultant growth rate  $W(t)$  is given as

$$W(t) = W_a + W_f + \frac{K}{W_a + W_f} \frac{\omega \epsilon z_0}{qt} \frac{\sqrt{2}}{\pi} E \tag{5}$$

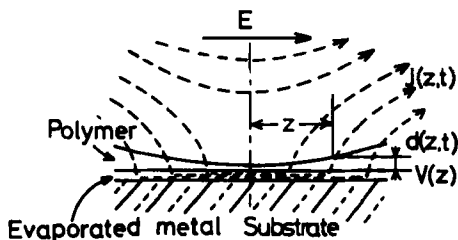


FIG. 2. Current distribution on the substrate.



where  $\omega$  is the angular frequency,  $\epsilon$  is the dielectric constant of the film,  $2Z_0$  is the width of the evaporated metal in the direction of the applied electric field,  $t$  is the discharge period, and  $E$  is the electric field in the plasma region. The third term on the right-hand side of Eq. (5) is the component due to the effect of stray capacity.

### Experimental Results

Experimental results are shown in Figs. 3, 4, and 5. The thickness increases with gas pressure up to 0.5 Torr, while it falls at the higher pressure as shown in Fig. 3. Our model can be applied to the pressure range greater than 0.5 Torr.

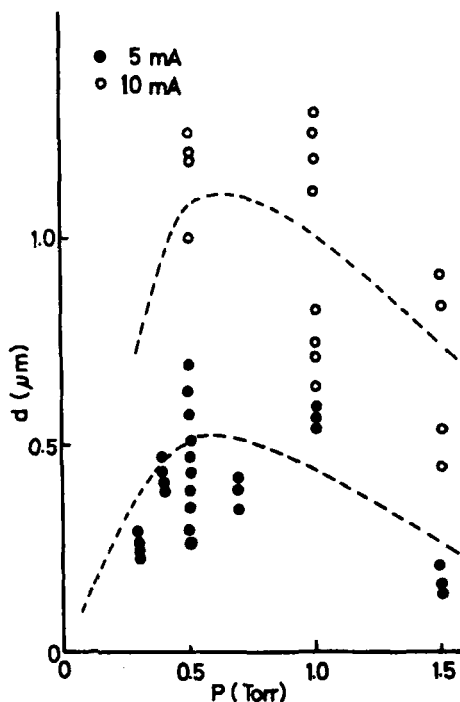


FIG. 3. Relation between the thickness ( $d$ ) and the gas pressure ( $p$ ). Polymerization conditions: 5 kHz, 4 min.

## Empirical equations

$$d(t) = 6t + \frac{1800}{6} \ln \frac{t}{t_0} \quad (\text{\AA}) \quad (6)$$

and

$$d(f) = 300 + 1000f \quad (\text{\AA}) \quad (7)$$

are obtained from Figs. 4 and 5, respectively, where  $t_0$  is the time for forming a unimolecular layer of adsorbed monomer. The first term on the right-hand side of Eq. (7) gives an integration of  $W_a$  for time, resulting in  $W_a \approx 1$  to 2 ( $\text{\AA}/\text{sec}$ ). The first term on the

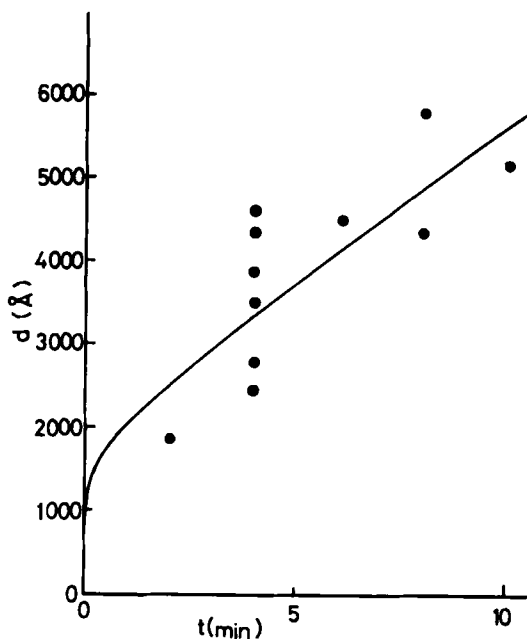


FIG. 4. Relation between the film thickness ( $d$ ) and the discharge duration ( $t$ ). Polymerization conditions: 0.5 Torr, 1 mA/cm<sup>2</sup>, 5 kHz.

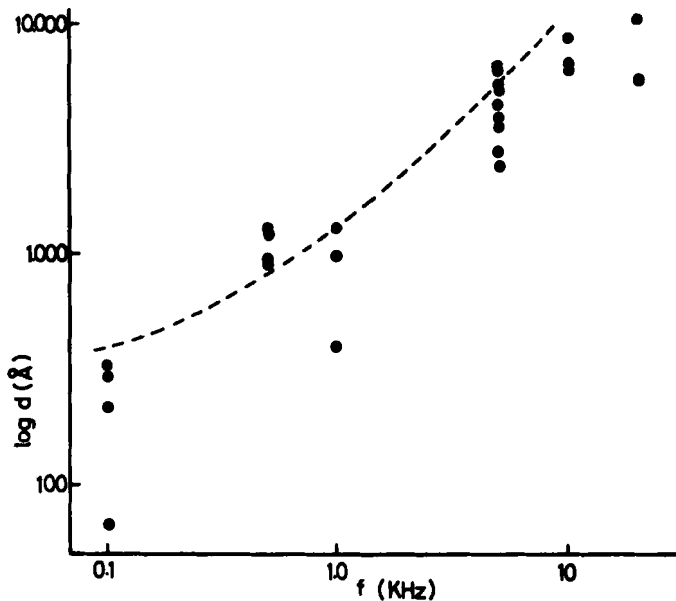


FIG. 5. Relation between the thickness ( $d$ ) and the frequency ( $f$ ). Polymerization conditions: 0.5 Torr, 1 mA/cm<sup>2</sup>, 4 min.

right-hand side of Eq. (6) gives the integration of  $W_a + W_f$  for time and thus  $W_f/f \approx 0.5$  to 1 (Å/sec kHz) is obtained. Comparing Eqs. (5) and (6), one obtains

$$\sqrt{2} K \omega \epsilon z_0 E / \kappa q = (1 \sim 2) \times 10^{-13} \text{ cm}^2$$

By substituting  $p = 0.5$  Torr,  $I = 5$  mA,  $B = 2$  cm,  $l = 1$  cm, and  $T = 300^\circ\text{K}$  as the experimental conditions, and  $\delta = 10$  Å,  $\mu_i/\mu_e \approx 10^{-4}$  and  $K = 10^{-6}$  as the assumed ones into Eq. (3), we can obtain the value of  $W_a/K$ . Then, by using the experimental value of  $W_a$  and supposing  $\rho = 1$ ,  $gn_\infty \approx 3$  to 6 is obtained. This value is in good agreement with Poll's value of 3.92 at 0.5 Torr.

Moreover, by supposing  $T \approx T_i$ ,  $T_e \approx 10^8$  K, and using the experimental value of  $W_f/f$ ,  $\lambda_s \approx 0.2$  to 0.4 cm is obtained from Eq. (4). This value is one order of magnitude larger than the mean free path of electron. This is probably due to the assumption that three transport processes are considered independently.

The experimental value of the component due to the stray capacity is examined as follows. Comparing the theoretical equation and the empirical one, the value of  $z_0E$  is smaller than 0.1 V, which corresponds to the case of  $z_0 = 0.1$  cm and  $E = 1$  V/cm. If we deduce the growth rate by considering the ion sheath along with the effect of stray capacity, this value of  $z_0E$  will become larger.

### Discussion

The growth rate of organic thin films by the low-frequency glow-discharge indirect method was, on the basis of Poll's theory, deduced by a phenomenological treatment in which the growth rate could be calculated by estimating the transport processes of electric charges. The present concept can also be applied to understand the growth rate in cases other than the indirect method unless the applied frequency is higher than an order of 1 MHz. In the case of dc glow-discharge, the growth rate is shown by the first term of Eq. (5). In the case of ac glow-discharge, the second term of Eq. (5) increases with an increase of frequency, and the third term of Eq. (5) has an effect on the growth rate when a metal film is evaporated on the substrate. At the higher frequency of discharge, the second and the third terms of Eq. (5) become small because of the effect of residual ions, and the component of diffusion of free radicals becomes more important.

Also, in the case of the electrodeless glow-discharge method, Eq. (5) can possibly be applied. On the other hand, in the case of direct method, the third term of Eq. (5) becomes the dominant growth mechanism.

## PROPERTIES OF GD FILM

In order to elucidate the molecular and morphological structures of GD film by the indirect method, NMR, ESR, and dielectric measurements were made.

### NMR Measurement

The results on GD films by the indirect method along with conventional polystyrene and styrene monomer are shown in Fig. 6. The NMR spectrum of a GD film by the indirect method is markedly different from those of conventional polystyrene and styrene monomer. The absorption at a chemical shift of 7 ppm due to protons in phenyl radicals [41] is observed in all three specimens, but the other parts of spectrum are quite different.

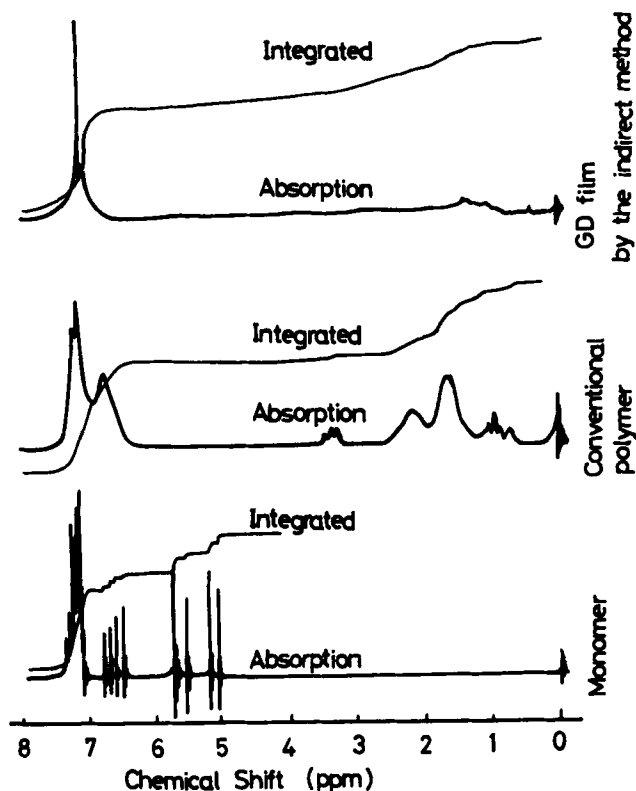


FIG. 6. NMR spectra of polystyrene formed by the GD-indirect method (0.5 Torr, 20 kHz,  $1 \text{ mA/cm}^2$ ). Conventional polystyrene and styrene monomer.

The NMR spectrum of the monomer is well understood [41], but the spectra of conventional polystyrene and of GD film are not clearly understood. In a comparison of the spectra of GD film and of polystyrene with that of styrene monomer, the following significant points may be noted.

Absorption for GD film by the indirect method is very weak in the whole range except at 7 ppm and is widely distributed from 0 to 7 ppm. The NMR spectrum for conventional polystyrene shows a few intense absorption peaks. Since the absorption spectrum will shift and be broadened by intra- and intermolecular interactions, the broad

spectrum observed on GD film by the indirect method suggests a three-dimensional mesh structure.

The NMR measurement for GD film by the direct method was not successful because the film was barely dissolved in benzene-d<sub>6</sub>.

### ESR Measurement

The ESR spectrum of GD film by the indirect method gave an isotropic ESR signal at  $g = 2.000 \pm 0.005$ . The spin density was estimated at  $\sim 3 \times 10^{16}$  spins/g, which was smaller than that of GD film by the direct method ( $\sim 5 \times 10^{17}$  spins/g) [39]. The temperature dependence of spin density and  $\Delta H_{\text{msl}}$  are shown in Fig. 7, where sample I was kept in air and sample II was sealed off at  $\sim 10^{-3}$  Torr. The ESR signal in the low-temperature region of heat treatment is possibly due to carbon radicals introduced in the polymerization process [39]. On the other hand, the increase of the signal intensity in the high-temperature region is attributed to oxygen radicals [39]. The carbon radicals thus remain at room temperature, and they will react with the oxygen in the air, resulting in the oxidation of the GD films.

### Dielectric Properties

Experimental values of the relative dielectric constant of GD films were 2.6 or larger. The value of  $\tan \delta$  was about 10 times as large as that of conventional polystyrene at room temperature and 1 kHz. The temperature dependence of capacitance  $C$  and  $\tan \delta$  at 1 kHz are shown in Fig. 8. Capacitance increased with a temperature rise above 50°C, and  $\tan \delta$  showed a peak near 50°C.

The heat treatment at 170°C in  $5 \times 10^{-5}$  Torr caused a several fold increase in capacitance, and after the heat treatment the peak of  $\tan \delta$  at 50°C disappeared. The heat-treated film by the GD indirect method exhibited a temperature dependence of  $\tan \delta$ , similar to the film by the direct method as shown in Fig. 9. The dielectric properties of the films by the GD direct method are slightly influenced by the heat treatment. This change in dielectric properties with heat treatment suggests the evaporation of molecules of smaller molecular weight involved in the GD film by the indirect method. However, the film manifested no symptom of melting, even at 200°C, in contrast to conventional polystyrene. Most molecules are therefore possibly highly cross-linked, as suggested from the NMR study.

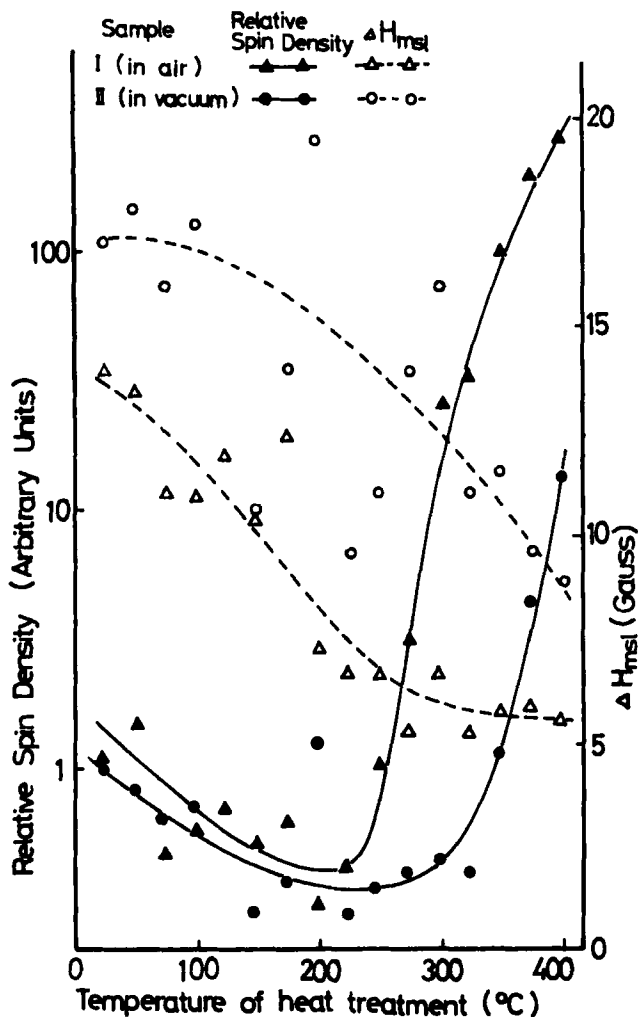


FIG. 7. Effect of heat treatment on spin density and line width of ESR. Polymerization conditions: 0.5 Torr, 1 mA/cm<sup>2</sup>, 5 kHz.

### CONCLUSION

The growth rate of thin polymer films by the glow-discharge indirect method was calculated theoretically by estimating the transport process of electric charges. These results agreed well qualitatively with the experimental results. From NMR, ESR, and dielectric measurements it was suggested for the film

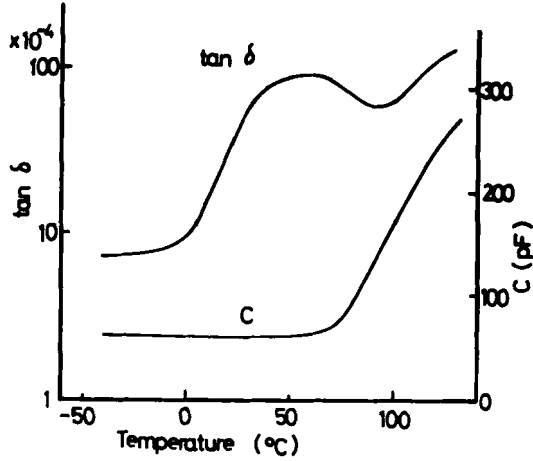


FIG. 8. Temperature dependence of  $C$  and  $\tan \delta$ . The measurement was done from low temperature to high temperature. Polymerization conditions: 0.5 Torr, 1 mA/cm<sup>2</sup>, 5 kHz, 20 min.

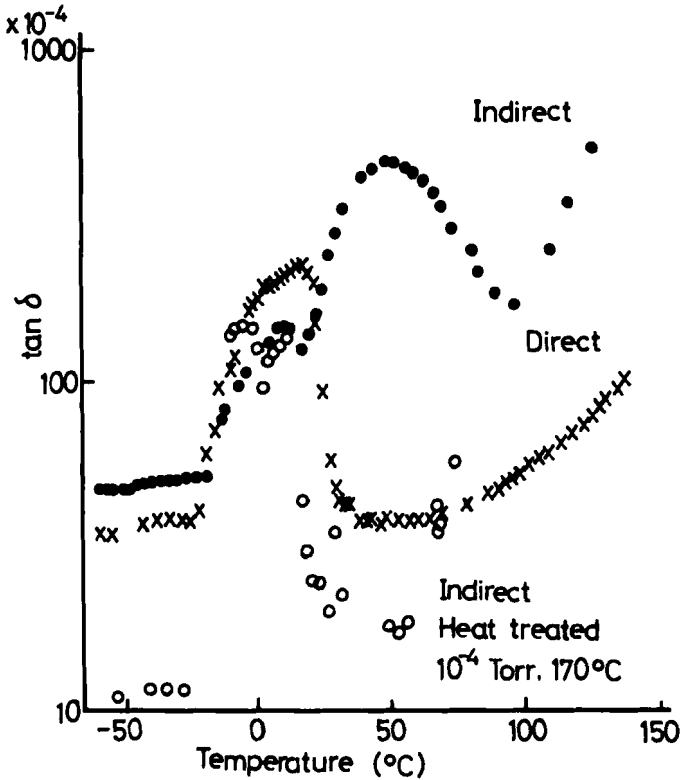


FIG. 9. Effect of heat treatment on  $\tan \delta$ .



structure that small molecules and free radicals remained in the film, but most molecules had a three-dimensional mesh structure. Therefore, heat treatment or a corresponding process should be employed in order to remove the free radicals and the small molecules to stabilize the GD film.

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