Gas Discharge in Hexamethyldisiloxane

Y. SEGUI and BUI AI, *Laboratoire de Génie Electrique de l'Université Paul Sabatier, Equipe "Matériaux Diélectriques" Associée au C.N.R.S., 31000 Toulouse, France*

Synopsis

A method of making thin polymer (polystyrene and polysiloxane) films by glow discharge is described. The thickness of the films varies between several hundred angstroms and a few microns. The parameters of the method are studied: pressure, frequency, current density in the discharge, and discharge time. An interpretation of the physical phenomena is given, and we show that it applies qualitatively to the two polymers studied. An infrared spectrometric analysis of the product obtained shows that it differs little from the product obtained by chemical means and that, for polysiloxane, the most probable configuration is that of a linear polymer. Thermostability is studied, and we show that the polymer does not suffer any serious damage up to temperatures of 400°C applied for about 10 hr. The possibility of obtaining films of several thousand angstroms and with adequate temperature stability make it possible to use polymers in the insulation and the passivation of semiconductor components.
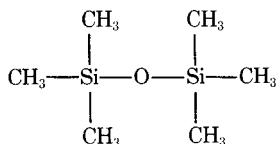
INTRODUCTION

With a view to using organic polymers in the field of microelectronics, we have developed the synthesis of thin polymer films whose thickness varies between 300 Å and several microns.

Very early, in 1950, Goodman[1] observed a solid dielectric deposit after an electrical discharge in a monomer gas. More recently, Gregor[2] and Smolinsky[3] synthesized several polymers in this way and investigated the electrical and optical properties of the substance obtained. Lastly, we can mention the work of Carchano,[4] who gave an interpretation of the mechanism of polymerization by electrical discharge.

The polymerization is obtained by creating an electrical discharge between two electrodes situated in an atmosphere of monomer gas at a pressure of the order of 0.3 torr. Under the action of the discharge, we see that a solid deposit is formed on the electrodes. According to the authors, this method varies slightly especially with the frequency of the discharge which goes from direct current[5] to several KHz[6,7] and to several MHz.[8,9]

Our aim in this paper is to clarify the conditions of growth of a polymer synthesized from hexamethyldisiloxane (HMDS):

$$CH_3\text{---}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}\text{---}O\text{---}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}\text{---}CH_3$$
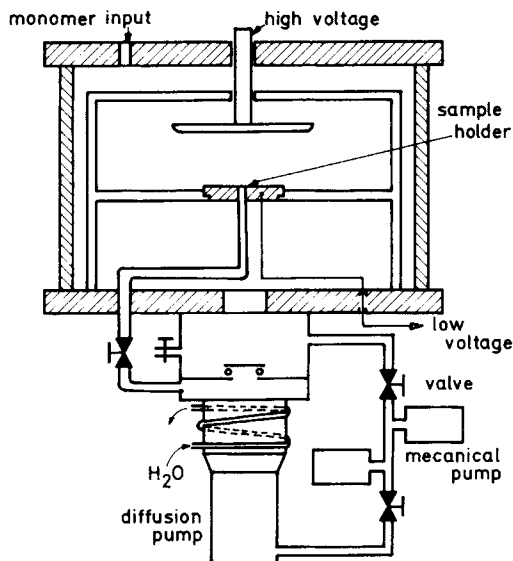
Fig. 1. Experimental apparatus for deposition of thin films.

This should allow us to define the formation mechanism. Finally we will proceed to the infrared analysis of this substance.

EXPERIMENTAL APPARATUS

The apparatus (Fig. 1) is composed of a bell jar in which it is possible to create a vacuum of 10^{-6} torr, a high voltage electrode, and a sample holder (the detail of which is given in Fig. 2). In addition, there is an input for the monomer controlled by a needle valve.
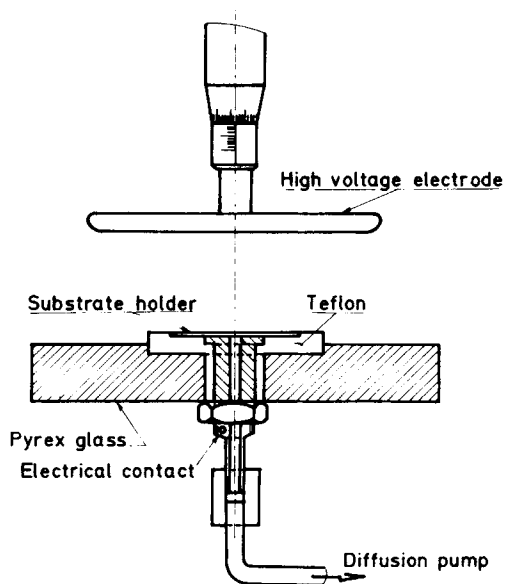

Fig. 2. Sample holder.

The pressure is measured either by a thermocouple gauge or by a diaphragm-type capacity torrmeter. The advantage of the latter is that it furnishes an indication independent of the nature of the gas in the bell jar. The position of the sample is assured by a Pyrex glass disc in which a Teflon sample holder is lodged. These materials were chosen because they are stable under the action of the electrical discharge and there is no danger of them being degraded by giving out undesired groupings. An opening connected with the diffusion pump is made in the sample holder. This makes it possible to maintain the sample in place by aspiration.

GROWTH OF POLYMER LAYERS

The growth mechanism suggested by Carchano in the case of styrene[4] is the following: (1) monomer molecules are adsorbed at the sample surface; (2) the particles which are ionized in the discharge and accelerated by the fields strike and break bonds on the adsorbed molecules; (3) these broken bonds allow other molecules of the monomer to be linked together.

Research shows that the active particles in the discharge are the ions and their energy is sufficient to break bonds in the monomer. In this way, a certain number of experimental results can be explained:

1. The thickness of the film is a function of the discharge duration.

2. The increase of the thickness as a function of the discharge current is at first linear, until it reaches saturation. In fact, when all the molecules adsorbed at the surface are struck by the ions, an increase in this number of ions no longer increases the number of broken molecules.

3. There is an initial increase in the growth rate with pressure P because then the number of monomer molecules increases. Above P_{max}, there is a decrease because the kinetic energy of the ions is considerably decreased by the collisions.

We see that this theory is not restrictive to a single type of monomer but that it should apply to numerous substances. The only difference will be in the computation of the energy of the ions in the discharge and in the energy they will have to furnish in order to break the bonds of gas. If the synthesis from HMDS gives qualitatively the same results as a synthesis from styrene, we can conclude that this theory is valid.

EXPERIMENTAL RESULTS

Figure 3 shows the variation of the growth rate with the HMDS pressure. A strong increase can be seen up to pressures of 0.5 torr. The results published on styrene showed an increase up to about 0.3 torr, then an exponential decrease. The equation showing the number of electrons whose energy is superior to the excitation energy of the molecules can be written (according to Loeb[10] and Von Engel[11]:

$$n_e(X) = \frac{4c}{(2\pi m)^{1/2}} \left(\frac{M}{m}\right)^{1/2} (0.43eX)^{1/2} n \left[\frac{E_{ex}}{\lambda^{1/2}} + 0.57FeX \left(\frac{\lambda M}{m}\right)^{1/2}\right] \exp$$

$$-\frac{3}{2} \frac{E_{ex}}{0.43eX\lambda \left(\frac{M}{m}\right)^{1/2}}$$
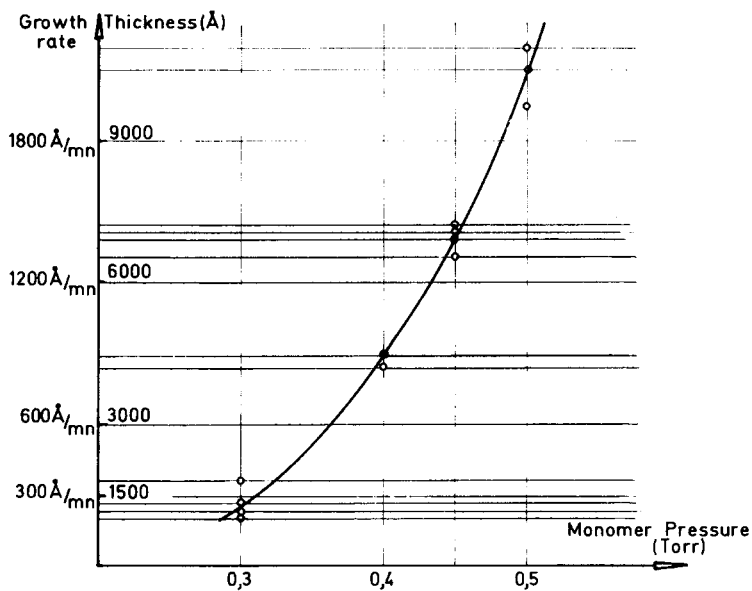
Fig. 3. Plot of polysiloxane thickness as a function of monomer pressure in the bell jar: discharge current, 0.17 mA; voltage, 340 V; duration, 5 mn; frequency, 2 KHz; temperature, 23°C.

where M and m are the mass of the molecule and the mass of the electron; X is the field in the discharge; E_{ex} is the excitation energy of the molecule; and λ is the mean free path. Equation (1) can be written as

$$n_e(X) = n[\alpha p^{1/2}X + \beta p^{-1/2}X^2] \exp - \left(\frac{\gamma}{M^{1/2}} \cdot \frac{P}{X}\right) \qquad (1)$$
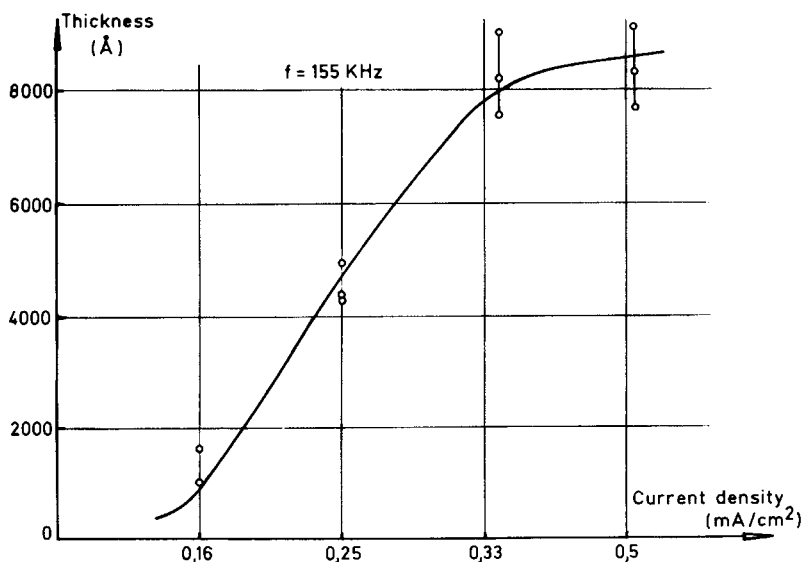

Fig. 4. Plot of polysiloxane thickness as a function of discharge current: voltage, 340 V; duration, 5 mn; frequency 155 KHz; monomer pressure, 0.35 torr; temperature, 23°C.
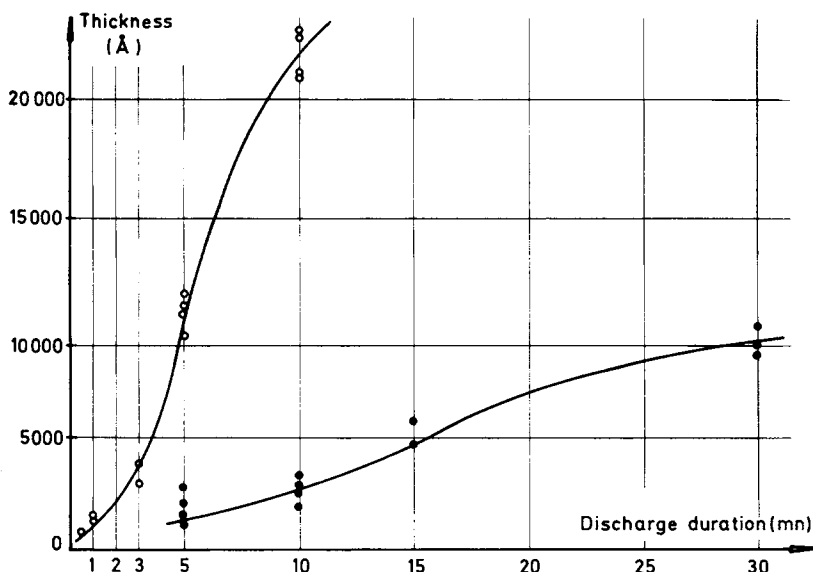
Fig. 5. Plot of polysiloxane thickness as a function of the duration of the discharge: discharge current, 0.17 mA; frequency, 2 KHz; temperature, 24°C; voltage, 340 V; pressure, (O) 0.5 torr, (●) 0.3 torr.

where p is the pressure which is inversely proportional to the mean free path and α, β, and γ are constants depending on M, m, and E_{ex}.

In the case of styrene, the molecular weight of which is 104, the term exp $-(\gamma P/M^{1/2}X)$ prevails only when $p \geqslant 0.3T$.

In the case of HMDS, whose molecular weight is 162, this term will have to be taken into account only for pressures superior to 0.7 torr because the multiplication factor is weaker. Below 0.7 torr, we are in a situation where the growth is governed by the number of molecules adsorbed on the substrate. This number is a increasing function of the density of the molecules in the bell jar, that is, of the pressure. In the pressure range explored, it is thus correct to see an increase in the growth rate with pressure.

Figure 4 shows the variation of growth rate with current density. We see a saturation beginning with a current density of 0.35 mA/cm^2. This value corresponds to the moment when all the adsorbed monomer molecules are activated by the discharge ions. An increase in the discharge current, then, cannot create more favorable sites for polymerization. The value of the saturation current is significantly the same as that obtained with styrene (0.45 mA/cm^2).

Figure 5 shows some growth curves in function of the discharge duration. The essential difference from results already published for other monomers[4] is that there is no longer linearity between thickness and time. The range of time on which we worked extends up to 30 mn. We notice two zones of nonlinearity, one toward long times, the other in the first instants of the discharge. The theory set forth by Carchano anticipated a linear dependence. However, the contradiction is only apparent; in fact, the voltage considered here is the voltage between the substrate and the high voltage electrode, whereas the important parameter is the voltage between the surface of the

polymer already deposited and the high voltage electrode. While the former remains fixed in time, the latter decreases with time. Under our experimental conditions, the decrease can be as high as 50% of the applied voltage, and for lower frequency could lead to the extinction of the discharge; this situation happens especially under d.c. conditions.

For the nonlinearity found during short periods of time, it is necessary to bring in the B.E.T. theory of adsorption.[12] This theory defines the kinetics of adsorption of molecules on a given substrate and, proceeding from there, the growth should be linear with time. In fact, the difference between the first instants of growth and the later is that, at the beginning, adsorption occurs on the silicon substrate and later on the places remaining available on the substrate and also on the polymer which is already constituted. Thus, the law of growth changes as long as the totality of the substrate is not covered with polymer. The numerical data do not exist in the case of HMDS or similar materials, and we cannot give a quantitative interpretation.

ANALYSIS OF THE PRODUCT OBTAINED

Figure 6 represents the infrared spectrum of a layer obtained from HMDS. We have more particularly taken the work of Wright and Hunter[15] as a reference to determine the peaks of absorption. These authors have analysed poly(methylsiloxane) of various molecular weights, linear, cyclic, or branched.

The C—H stretch vibration lies at 2960 cm^{-1}, exactly the characteristic position of methyl groups in hydrocarbons; but here its intensity is weaker.

Near 2150 cm^{-1}, we find a band absent from the HMDS spectrum. It could be due to R_3Si—H links in which R would be CH_3—Si—O (giving 2175 cm^{-1}) or CH_3—O— (giving 2203 cm^{-1}).

The C—H bending vibration of Si—(CH_3) group lies near 1400 cm^{-1}, close to those of hydrocarbons.

The so-called methyl rocking vibration of the dimethyl group Si—$C(CH_3)_2$ appears at 1260 cm^{-1}, while that of the trimethyl group occurs at 1250 cm^{-1}.

In the 1000–1100 cm^{-1} range occurs the strongest band of this spectrum. It involves the stretch vibration of the Si—O linkage.

At 840 cm^{-1} occurs the strong band due to the stretch vibration of the Si—C linkage in Si—$(CH_3)_3$. The same vibration gives a band at 800 cm^{-1} for Si—$(CH_3)_2$ groups.

The peaks involving a linkage with the Si atoms give a very strong absorption. This is due to the important ionic character of silicon bonds. Indeed, the intensity of the absorption band is proportional to the charge $|Q|$ located on the atoms. This fact has been well shown by Wright and Hunter[13] who give the ratio of the ionic character of the Si—O and C—O bond which is exactly the same as the ratio of the intensities of the Si—O and C—O peaks. From this analysis, we can draw some conclusions about the growth and structure of our layer.

It can be seen from the work of Wright and Hunter that the Si—C stretch band of the group —O—Si—$(CH_3)_3$ does not exist in the case of a cyclic poly(methylsiloxane). Moreover, the intensity of this band is weaker than those of the groups Si—$(CH_3)_2$; and by comparison with the results of Wright and Hunter, the length of the skeleton could be larger than those of hexasiloxane.
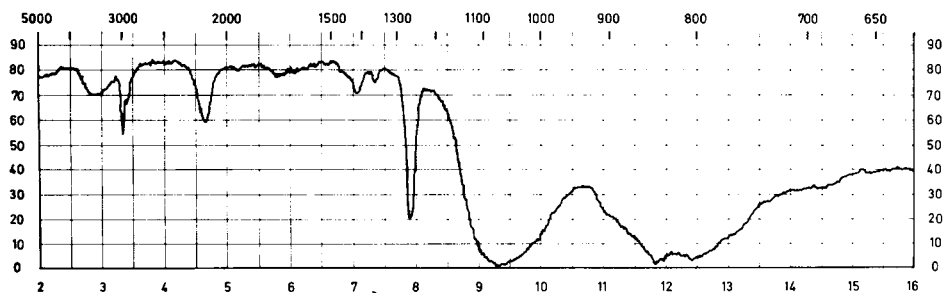
Fig. 6. Infrared spectrum of polymer made from hexamethyldisiloxane.

However, we cannot conclude that any cyclic form exists in our material because, unfortunately, the vibration bands of Si—O, both in its cyclic or linear form, lie in the 1000–1100 cm^{-1} range.

The peaks occurring near 2100 cm^{-1} could be atributed to R_3Si—H links; in this case, we should have a branched polymer. Agreeing with this is the fact that the C—H stretch vibration band at 2960 cm^{-1} is weak.[14]

The growth of this material is obtained by addition of $(CH_3)_2Si$—O groups. We cannot determine at this time which are the bonds broken by the ions of the discharge; but the fact that a branched polymer is obtained is not surprising because each of the Si—C bonds can be broken.

STABILITY AS A FUNCTION OF TEMPERATURE

Thermal stability is a very important property in the industrial applications of polymers. The evolution in function of thermal treatments is followed by infrared spectra. Thermal treatments were performed in a nitrogen atmosphere to avoid oxidation. A noticeable degradation threshold is reached after exposure to 450°C for 144 hr. Between the ambient temperature and 450°, we observe the following modifications: (1) The absorption band corresponding to the Si—H links disappears. (2) The absorption bands corresponding to Si—$(CH_3)_3$ links decrease in intensity. Wright and Hunter have shown this fact when the size of the polymer increases; in our case, it could be ascribed to a desorption of products which have not contributed to the addition. A measurement of weight loss could confirm this assumption.

CONCLUSIONS

This paper shows how polymers whose thickness varies between a few hundred angstroms and several microns can be obtained. The parameters of the fabrication method were studied and an interpretation of the experimental results obtained on various types of polymers was suggested. Quantitative evaluations verify the differences of growth kinetics between the different polymers. Analysis by infrared spectroscopy showed this polymer was linear and presented the same absorption bands as the polymer synthesized by purely chemical means. The polymer made by glow discharge is stable up to temperatures of 400°C applied for periods as long as 20 hr. This point is important for the use of polymers as insulator in electrical circuits or electronic components.

References

1. J. Goodman *J. Polym. Sci.*, **44**, 551 (1960).
2. L. V. Gregor, *Thin Solid Films*, **2**, 235 (1968).
3. P. H. Tien, G. Smolinsky, and R. J. Martin, *Appl. Optics*, **11**, 637 (1972).
4. H. Carchano, Thesis, Université Paul Sabatier, Toulouse, 1973.
5. G. L. Gallet, R. Nannoni, and P. De Valence, *Onde électrique*, 515 (Feb. 1970).
6. A. Bradley and J. P. Hammes, *J. Electrochem. Soc.*, **110**, 15 (1963).
7. J. Morris and A. Charlesby, *Eur. Polym. J.*, **2**, 177 (1966).
8. A. R. Denaro, P. A. Owens, and A. Crawshaw, *Eur. Polym. J.*, **4**, 93 (1968).
9. B. Vuillermoz, private communication.
10. L. B. Loeb, *Basic Process in Gaseous Electronics,* University of California Press, 1961.
11. A. Von Engel, *Ionised Gases,* Clarendon Press, New York, 1955.
12. S. Brunauer, P. M. Emmett, and E. Teller, *J. Amer. Chem. Soc.*, **60**, 309 (1938).
13. N. Wright and M. J. Hunter, *J. Amer. Chem. Soc.*, **69**, 803, (1947).
14. L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* Methuen, London, 1964.