

A Scanning Electron Microscope Study of Plasma-Polymerized Organosilicon Films Suitable for use as Lightguides. A Determination of the Cause of Signal Attenuation

L. F. THOMPSON and G. SMOLINSKY,
Bell Laboratories, Murray Hill, New Jersey 07974

Synopsis

The scanning electron microscope was used to evaluate the optical quality of a plasma-deposited organic film. A major source of signal attenuation in lightguide films results from scattering by microscopic embedded spheres. The spheres are produced in the gas phase, and their size and population density are a function of the substrate surface and the rate of film formation. For all systems studied, the number of spheres increase with increasing rate. High-quality films were deposited more easily on silicon, silicon dioxide, tungsten, and glass than on Nichrome or β -tantalum. Gold, copper, and titanium surfaces proved more difficult, while aluminum was the most intractable material encountered. The rate of film growth usually increased with an increase in power input for any ratio of total pressure-partial pressure of monomer. Spheres were essentially eliminated or their number reduced to a tolerable level by a proper choice of reaction conditions.

INTRODUCTION

The potential use of plasma-deposited organic films as dielectric coatings or encapsulants for microelectronic devices has long been appreciated.¹ More recently,² an interest has developed in using these materials as laser lightguides in optoelectronic devices. In order for a film to be useful as a lightguide, it must exhibit extremely low scattering losses (less than 0.5 db/cm). A low-loss polymer film must therefore have all the following characteristics: Its surface must be smooth relative to the wavelength of light; it must be amorphous, i.e., contain no crystalline regions; it must not contain inclusions which can scatter light nor must it have regions with abrupt differences in refractive index.

Films produced in a glow discharge can fulfill all these requirements.² However, it has been observed that under certain conditions, polymerization occurs in the vapor phase leading to the production of submicron spheres which become embedded in the film matrix and may roughen the film surface. The optical quality of the film is significantly impaired so that it is useless as a lightguide if the number of spheres covers more than 0.1% of the area ($<10^5/\text{cm}^2$).

The rate of film deposition directly influences the sphere population and its size. Although several parameters affect the rate such as power input, partial pressure of monomer, total system pressure, and position of the substrate in the reaction chamber, the sphere population appears only to depend on the rate of film growth and to be independent of the rate-controlling parameter. The substrate also affects the number of spheres, even though the rate of film growth is unaffected.

Since the optical quality of a film is inversely proportional to its rate of deposition, one would like to know for a given monomer the highest allowable rate of deposition on a given substrate that will lead to a usable lightguide. A direct optical measurement of scattering losses in a film is a difficult, time-consuming experiment,² and impractical for any study requiring numerous loss measurements. However, by using the scanning electron microscope (SEM), we were able to determine what physical imperfections in the film were mainly responsible for the observed signal loss and hence to develop a rapid, semiquantitative technique for evaluating polymer films for suitability as lightguides.

We report here an SEM study of films prepared from tetramethylsilane (TMS), hexamethyldisiloxane (HMDS), and vinyltrimethylsilane (VTMS) and deposited on a variety of metallic and nonmetallic surfaces.

EXPERIMENTAL

The films evaluated in this study were prepared in an apparatus previously described by Vasile and Smolinsky.³ It essentially consisted of circular, congruent parallel electrodes positioned horizontally and separated by 4 cm in an enclosed system which could be pumped and/or fed with gases under controlled conditions. The lower electrode was connected to the output of a 13.56-MHz RF generator through an impedance matching network. The upper electrode was held at ground potential. Substrates upon which polymer was to be deposited were placed on the lower electrode. Films were prepared from three monomers, each containing the element silicon: hexamethyldisiloxane (HMDS), vinyltrimethylsilane (VTMS), and tetramethylsilane (TMS). The three gases helium, argon, and hydrogen were used as co-gases.

The effects of such variables as power input, total pressure, partial pressure of monomer, and the co-gas on the rate of film growth and optical quality were examined. For a given set of conditions, a rate of film growth on the substrate was determined with an accuracy of $\pm 5\%$ by measuring the weight gained by 25 cm² of thin aluminum foil. Note that this rate is not a measure of the overall kinetic rate of polymerization in the chamber but only a measure of film growth rate on the substrate.

Films were prepared from HMDS (0.05 torr) and argon, helium, or hydrogen (0.15 torr) at 100 watts on aluminum (Al), copper (Cu), gold (Au), Nichrome (NiCr), silicon (Si), silicon dioxide (SiO₂), beta-tantalum (β Ta), titanium (Ti), and tungsten (W). Films were also prepared from VTMS

(0.1 torr) and argon (0.2 torr) at 150 watts on Al, Cu, Au, NiCr, Si, SiO₂, and W. The films on the substrates were examined with a Cambridge Mark II SEM. For each film, four electron micrographs of the surface were taken at random locations, and the number of particles or spheres present in each picture was counted. The average for the four pictures was converted into a population density of spheres per square centimeter of surface area. Micrographs of fracture edges of polymer films indicated that the spheres are uniformly distributed from top to bottom.

A power range of 50 to 200 watts was employed to prepare both HMDS and TMS films. In addition, films were prepared at 100 and 150 watts from pure TMS over a pressure range of 0.1 to 0.4 torr. TMS films were also prepared in the presence of different concentrations of argon at constant total pressure and power.

RESULTS AND DISCUSSION

Scattering losses for films with essentially zero sphere populations were found to be several orders of magnitude less than for films with average to high sphere populations.² From these observations it was concluded that the spheres were a significant cause of signal attenuation. The spheres probably result from vapor-phase polymerization of monomer, and their concentration is a function of the substrate surface and the rate of film growth.

In Table I, the surface effect on the population density of spheres is presented. Conditions which give apparently sphere-free films on silicon, silicon dioxide, and tungsten give enormous concentrations of spheres on aluminum while producing moderately high (Cu, Au, Ti) to somewhat lower (NiCr, β Ta) concentrations on other surfaces. Figures 1 to 4 are electron micrographs of HMDS films deposited simultaneously on Al, Au,

TABLE I
VTMS and HMDS Films Deposited on Different Surfaces^a

Surface ^b	(Number of spheres/cm ²) $\times 10^{-6}$			
	HMDS/Ar	HMDS/He	HMDS/H ₂	VTMS/Ar
Aluminum	7.6	4.0	8.0	6.0
Copper	1.0	0.1	2.0	2.0
Gold	0.5	0.2	0.1	1.0
Nichrome	0.08	0	0.8	0
Silicon	0	0	0	0
Silicon dioxide	0	0	0	0
β -Tantalum	0.2	0.1	0.2	—
Titanium	0.3	0.1	0.2	—
Tungsten	0	0	0.01	0

^a VTMS films prepared at 0.1 torr VTMS and 0.2 torr argon at 150 watts; HMDS films prepared at 0.05 torr HMDS and 0.15 torr inert gas at 100 watts.

^b Films were deposited simultaneously on each surface in the same run for each set of conditions.



Fig. 1. HMDS polymer film deposited on aluminum.

NiCr, and Si, respectively. These pictures are examples of the differences in the quality of the polymer film on the various substrates. The film deposited on Al (Fig. 1) is useless as a lightguide material since the polymer is exceedingly inhomogeneous, consisting entirely of approximately 1-micron spheres of polymer. On the other hand, the film on Si (Fig. 4) is apparently perfectly homogeneous and should be an excellent lightguide.² Note that the small white dots and apparent fine structure observed in the latter photograph are artifacts produced by accumulation of charge on the surface of the nonconducting film and do not represent the texture of the film. From Table I it is apparent that the nature of the inert gas used in preparing the HMDS films does not significantly affect the sphere density found on the various surfaces, nor does the ranking of the surfaces seem to be affected by the monomers employed, either HMDS or VTMS. Aluminum always is associated with exceedingly poor-quality films, while silicon, silicon dioxide, and tungsten are associated with exceedingly high-quality films.

Although we see no obvious correlation between the physical or chemical properties of the various metals and the sphere population observed, we would like to offer the following rationalization for our experimental

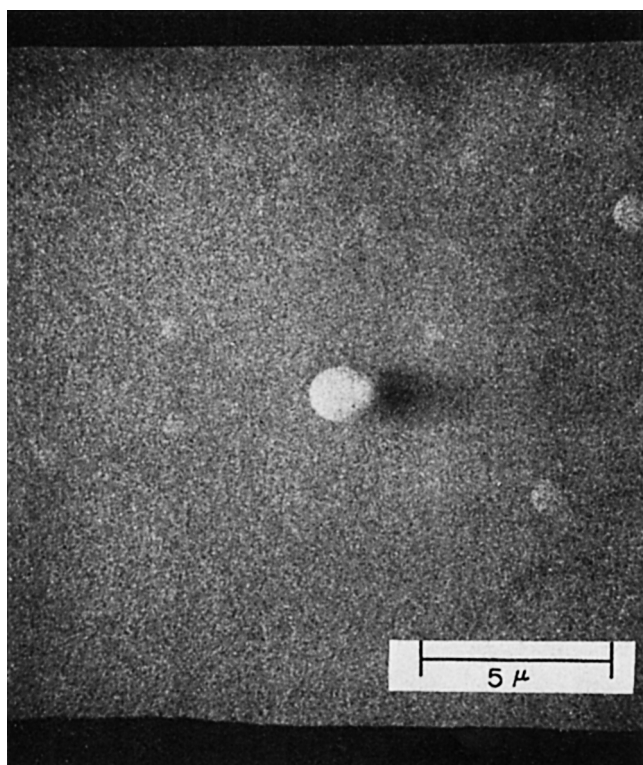


Fig. 2. HMDS polymer film deposited on gold.

results: Any object placed in a homogeneous plasma-glow perturbs the plasma. Some materials cause a significant decoupling between the RF field and the gas; therefore, certain metals would disturb the plasma in their immediate vicinity, but because of the relatively small size of the sample the remainder of the plasma would be unaffected, and the overall bulk effect would be negligible. However, in the immediate vicinity above this metallic substrate, the concentration of ionic and reactive species could be so markedly altered as to affect the rate of vapor-phase polymerization in this region of the plasma. Thus we would find a variation in sphere population as a function of the substrate compositions.

The weight of VTMS polymer deposited per minute for a 10- and 100-min run was found to be identical on Al and SiO₂ even though these substrates show enormous differences in sphere population for films deposited simultaneously in the same run (see Table I). Obviously, most of the polymerization reaction is occurring in the vapor phase above the aluminum while for glass the reaction is proceeding on the surface of the substrate. The rates of deposition for both VTMS and HMDS films were found to be 1.5 times faster in helium or hydrogen than in argon under conditions of equal partial pressure of monomer and the same total pressure and power input, respectively.

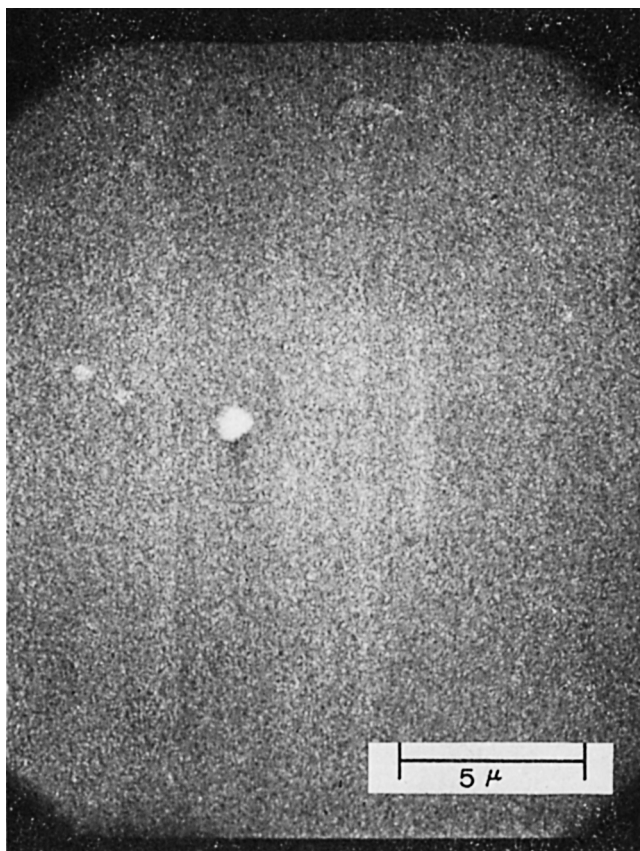


Fig. 3. HMDS polymer film deposited on titanium.

The fact that the rate of deposition of film affects the sphere population is shown by TMS film deposited on aluminum. Figure 5 shows a plot of sphere density versus rate for 13 different sets of reaction conditions. As the rate was increased by nearly an order of magnitude, the population density increased by a comparable amount. We repeat that the rate of polymerization is a function of power input, of partial pressure of monomer, and of total system pressure and that a given rate can be achieved by using different combinations of values for these variables. We emphasize that the sphere population is dependent only on the rate and not on how this rate was established.

Figures 6 through 10 show the dependence of film growth rate on the different variables. Figures 6 and 7 show a linear dependence of the rate with increasing power for HMDS and TMS films, respectively. One might also conclude from Figure 7 that for any power input an increase in pressure of monomer will result in an increase in the rate of film growth. However, this is not necessarily so, for we see in Figure 8 that the rate of film formation reaches a maximum, but a further increase in monomer pres-

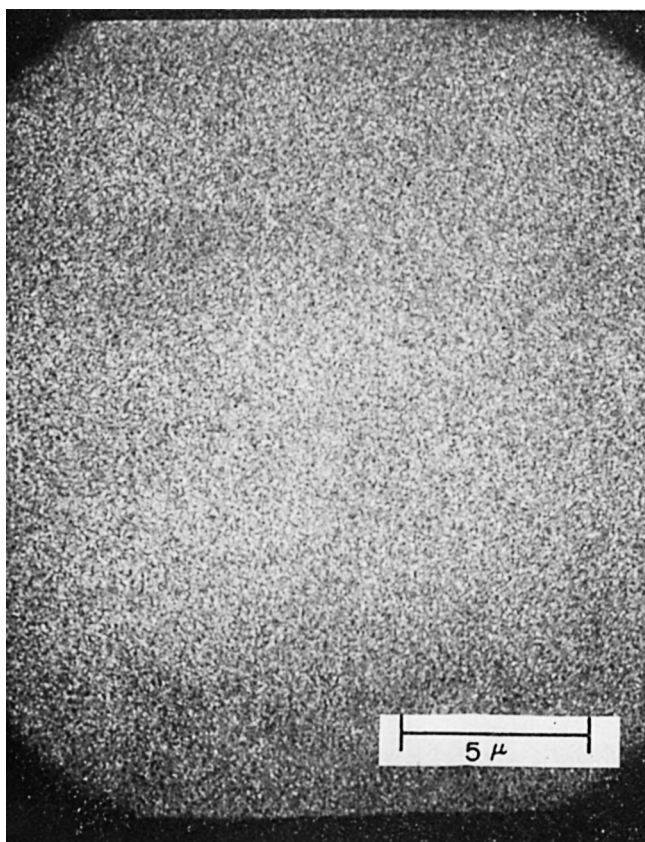


Fig. 4. HMDS polymer film deposited on silicon.

sure produces a sharp drop in rate. Figure 9 shows the same effect for VTMS film growth; that is, the rate initially increases with pressure but then falls off. Figure 10 points up the fact that the rate essentially remains constant at constant total system pressure and constant power level, even though the concentration of TMS is lowered from 100% to 20%. This latter behavior has also been observed for VTMS.³

These results can be rationalized by using naive plasma chemistry concepts. There are two parameters which affect the rate of a given chemical reaction in a discharge. They are related to, but are not always identical with, the familiar concept used by plasma physicists of the ratio of the electric field E to the system pressure P . The electric field and energy vary with the power input from the RF source. The E/P concept is probably only valid for monatomic and diatomic single-gas systems; for in polyatomic, co-gas systems the energy transfer mechanisms are much more complicated for the concept to be any more than just qualitatively useful. A uniform glow discharge at constant energy is sustained only over a particular pressure range. Below a critical pressure, the mean free path is

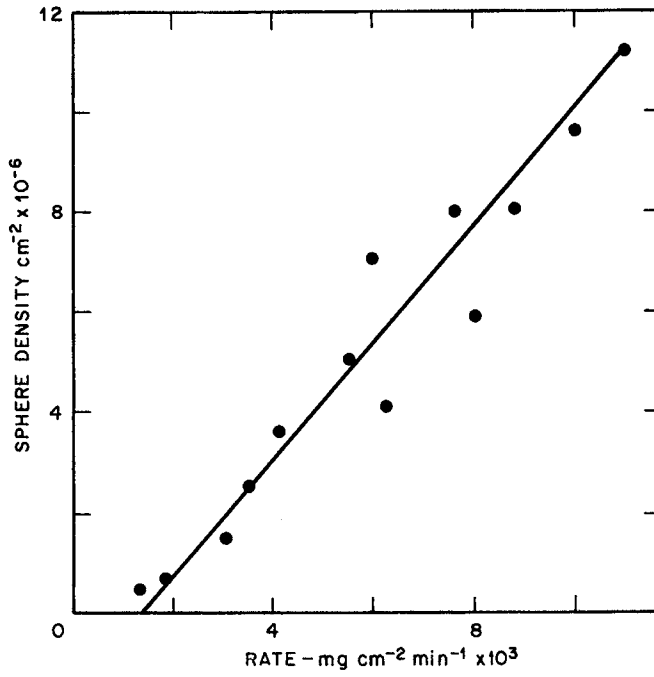


Fig. 5. Sphere density as a function of growth rate of TMS film.

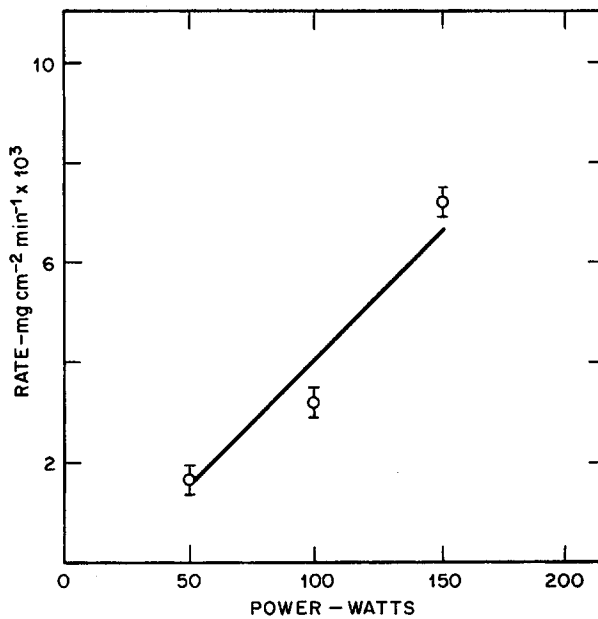


Fig. 6. Rate of film formation as a function of power for a mixture of 0.05 torr HMDS and 0.15 torr argon.

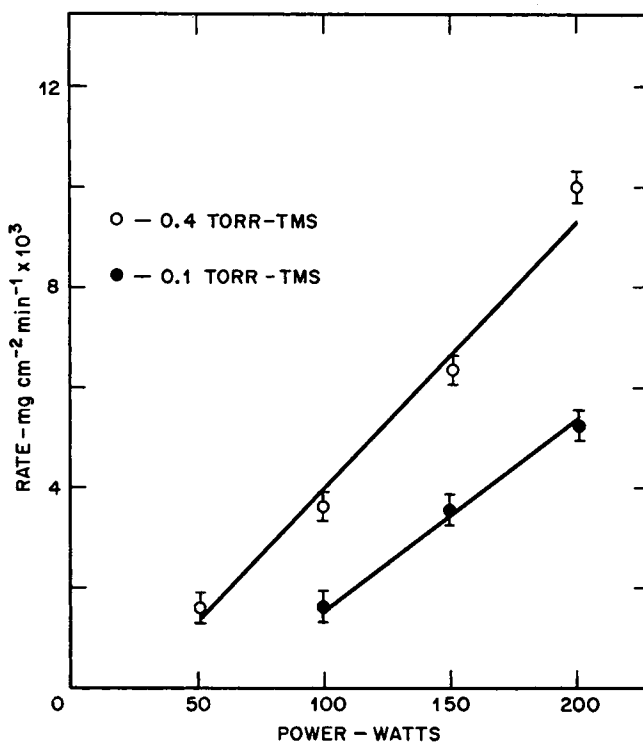


Fig. 7. Rate of film formation as a function of power for a constant total pressure of TMS.

too long to sustain the plasma, and above a certain pressure, the discharge will be quenched because collisions are so frequent that the electrons never gain sufficient energy to ionize the gas.

The same qualitative concepts may be used to formulate an argument about the effect of power input on the rate of film formation at a given pressure of organic vapor. In Figures 6 and 7, we see that there may be some lower limit of power required to sustain the reaction. The rate of film growth increases linearly with increasing power input, but eventually a level is reached at which a further increase in power produces only a negligible increase in rate.³ At this point, increasing the power does not cause any additional ionization of the gas and thus no additional increase in reactive species.³ It also follows that for a given power input, the partial pressure of monomer can be less than optimum for a maximum rate of ionization, and thus the rate will increase as the pressure of monomer increases at constant power (Figs. 7, 8, and 9). Figure 8 shows this latter effect as well as the effect of quenching the plasma by increasing the pressure and thus reducing the rate of film growth. Figure 10 shows the limiting effect on the rate of film growth of the ability of the system to produce the reactive intermediate. Here we see that at constant power and total pressure

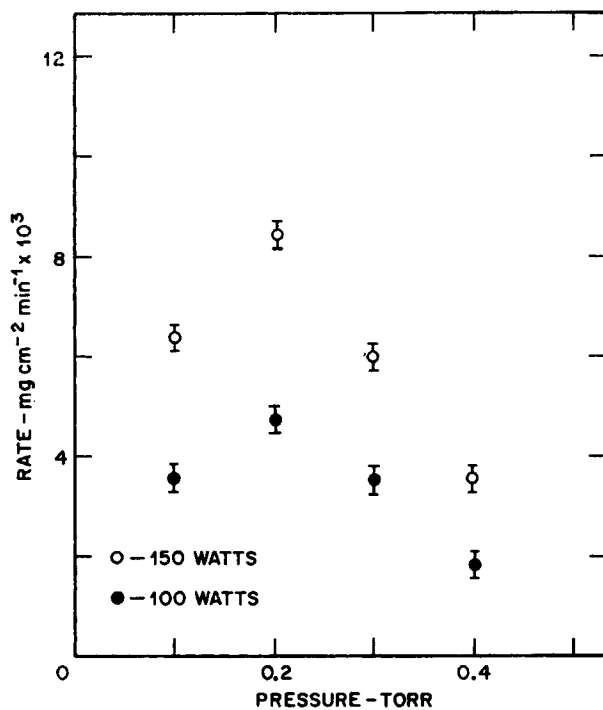


Fig. 8. Rate of film formation as a function of TMS pressure at constant power.

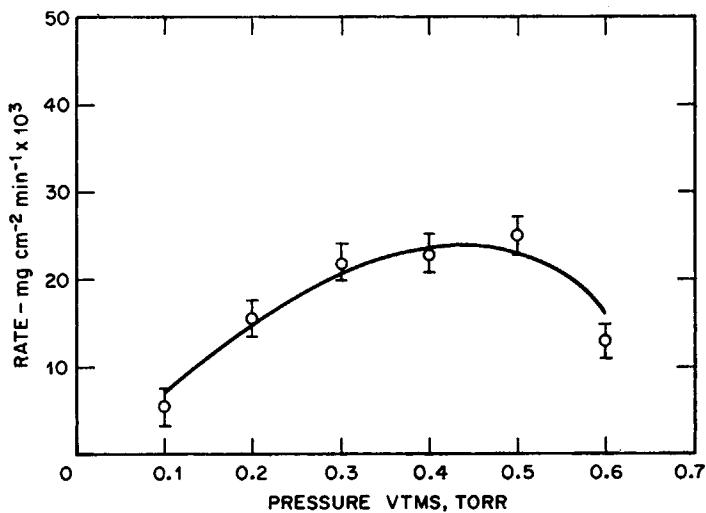


Fig. 9. Rate of polymer deposition as a function of monomer pressure at constant power (80 watts). From Vasile and Smolinsky.⁵

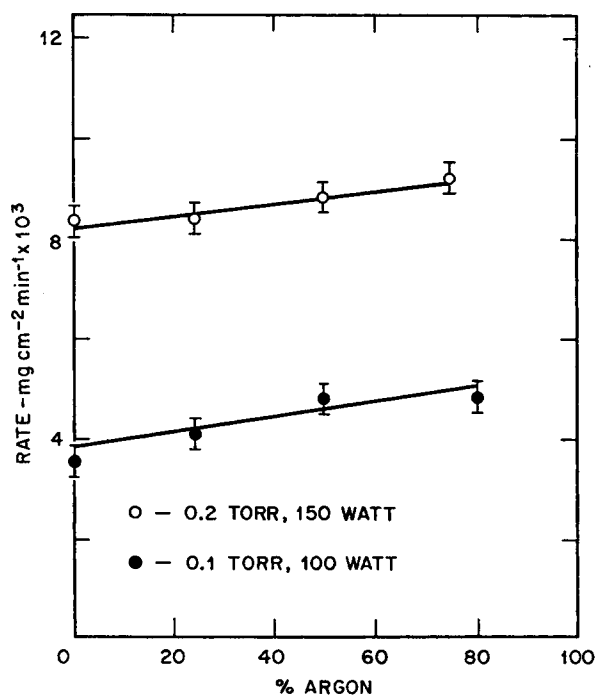


Fig. 10. Rate of film formation as a function of argon partial pressure for TMS and argon at constant total pressure and power.

(constant E/P), the rate remains essentially unchanged even as the concentration of monomer is reduced from 100% to 20%, indicating that the maximum concentration of reactive species is forming even at 20% partial pressure of monomer in this section of the reactor. We see then that the mechanism proposed accounts for a great many of the observed phenomena. It should be noted that the rates reported are not total kinetic rates of polymerization, but rather rates of film growth in only a section of the reactor. Hence these conclusions are only applicable to a given region in the reactor.

CONCLUSIONS

1. Scattering losses in plasma-polymerized lightguide films resulted from embedded microscopic spheres of polymer.
2. The number of spheres per unit area was determined with the scanning electron microscope. A prediction of the optical quality of films was possible.
3. The population of spheres was a function of reaction conditions, increasing with increasing rate of deposition.
4. The population of spheres was a function of the substrate surface. For identical reaction conditions, high-quality films were deposited on

silicon, silicon dioxide, tungsten, and glass; moderate-quality films, on Nichrome and β -tantalum; poor-quality films, on copper and titanium; exceedingly poor films, on aluminum.

5. The rate of film formation was a function of power input, partial pressure of monomer, and total pressure of the system.

6. Satisfactory lightguide films could be produced from all monomers by a proper selection of substrate surface and reaction conditions.

References

1. P. White, *Insulation*, **13**, 52 (1967); V. M. Kolotyskin, A. B. Gil'man, and A. K. Tsapuk, *Russian Chem. Rev.*, **36**, 579 (1967); A. M. Mearns, *Thin Solid Films*, **3**, 201 (1969).
2. P. K. Tien, G. Smolinsky, and R. J. Martin, *Appl. Opt.*, **11**, (March 1972).
3. M. J. Vasile and G. Smolinsky, *J. Electrochem. Soc.*, **119** (April 1972).

Received December 21, 1971