PLASMA POLYMERIZATION OF ARYLSILANES

Ivan Haller
IBM Thomas J. Watson Research Center, Yorktown Heights, NY 10598

ABSTRACT:

In contrast to the known plasma chemistry of other aromatic materials, aromatic silanes polymerize in a low-pressure, low-power RF plasma without the fragmentation of benzene rings. Infrared spectra indicate that the predominant structural features of the phenylsilane plasma polymer films are cross-linked polysilane chains with pendant phenyl groups. The degree of cross-linking increases with increasing substrate temperature.

1. INTRODUCTION

The formation of polymeric films in radiofrequency glow discharges have been reported[1,2] for numerous saturated and unsaturated organic compounds[1]. A common characteristic of these films is that their composition shows little resemblance to the monomeric starting material. In particular, it is well known that the benzene rings of aromatic starting materials suffer extensive fragmentation in the plasma, even under relatively mild discharge conditions, and the resulting polymers contain a large fraction of the total hydrogen in aliphatic C-H bonds[2-5].

It is also known[6-9] that SiH_4 plasmas deposit a polymeric silicon hydride ("hydrogenated amorphous silicon"), which is a useful semiconductor electronically dopable with conventional dopants for crystalline silicon.

We now find that aromatic silanes when subjected to an RF plasma result in transparent, insulating, thermally stable, aromatic polymer films. This paper discusses the structure of the polymeric films as elicited from infrared spectral evidence, and its implications on the plasma chemistry that leads to their formation. The physical properties of the polymeric films will be discussed elsewhere[10].

2. EXPERIMENTAL

Phenylsilane, diphenylsilane, and p-chlorophenylsilane were obtained from Petrarch Systems, Inc., and were purified by distillation [b.p 120° (at 760 torr), 132° (16), and 72-82° (56), respectively]. Toluene, benzene, and silane were "electronic" grade and were used as received. Disilylbenzene was prepared from fractionated (b.p. 110-114°C at 4 torr) bis-(trichlorosilyl)-benzene (Chemical Procurement Labs, Inc.) by $LiAlH_4$ reduction[11].

Substrate wafers (25 mm diameter) of silicon, α-Al_2O_3, or KBr disks were held on a thermostatted stainless steel pedestal and placed in a 45 mm diameter fused silica tubing in which the pressure and the flow rate were controlled by inlet and exhaust valves. RF power (13.6 MHz) was coupled through an external 3-turn coil. The radiated power was estimated by monitoring the forward and reflected power at the input of the match-box connecting the coil to the RF generator. Vapors of monomers were generally introduced into the plasma chamber from reservoirs containing the liquid which had been freed from air by repeated freeze-thaw cycles and evacuation. Diphenylsilane, however, whose vapor pressure is inadequate for the above procedure, was coated on glass rings filling a flow-through reservoir and was introduced by saturating a low pressure carrier gas of hydrogen or argon. Silane-phenylsilane mixtures were prepared in the gas phase at near atmospheric pressure, and at least 40 hours of diffusional mixing was allowed prior to introduction of the mixture into the plasma.

All polymer films described in later sections of this paper were deposited, unless otherwise noted, at a pressure of 0.10 torr and an RF power level just sufficient to maintain a very dim, doughnut shaped discharge above the substrate. This occurred at 1.5 to 2.0 watt power, and corresponds to a power density in the luminous part of the plasma of about 0.02 to 0.04 W/cm^3. In other experiments, plasma polymerization of arylsilanes was explored in the pressure range of 0.03 to 1 torr and a range of RF power input. Higher deposition rates were observed at higher pressures and power levels but these conditions were avoided to prevent precipitation of polymer in the gas phase resulting in fluffy deposits or cloudy films.

3. RESULTS

Aromaticity The infrared spectrum of a thin film of polymer formed from phenylsilane in an RF glow discharge at a pressure of $p = 0.1$ torr and a substrate temperature $T_S = 250°C$ is shown is the top trace in Figure 1. Similar spectra of polymers formed from toluene, and from a mixture of silane and benzene are shown in the middle and bottom traces, respectively. In the carbon-hydrogen stretching region, a striking difference is observed in the distribution of intensity in bands above and below 2980 cm^{-1}. In the lower two traces, most of the intensity appears in the 2910 at 2850 cm^{-1} bands corresponding to C-H stretches of sp^3 hybridized carbons. In the phenylsilane polymer, however, these lower frequency C-H stretches are much less intense than the 3040 cm^{-1} band indicative of aromatic C-H stretches. Considering that aliphatic C-H stretches generally have much higher oscillator strengths than aromatic ones[12], we conclude that the fraction of hydrogen that is bonded to aliphatic carbons is negligible in the phenylsilane plasma polymer.

Analogous results were obtained for disilylbenzene, p-chlorophenylsilane, and diphenylsilane. Table I compares the intensity ratios of aliphatic to aromatic hydrogen stretching vibrations in plasma polymers prepared under similar conditions from various precursors. The only source of aliphatic hydrogen in most cases is the fragmentation of the aromatic rings of the precursors in the plasma. It appears then that the fragmentation of the benzene rings in the plasma polymer formation is an insignificant process in the case of the arylsilanes, whereas it is a major one in aromatic compounds having no silyl substituents. Particularly noteworthy is the fact that the ratio is the highest in the polymer from a benzene-silane mixture indicating that an attack of silane fragmentation products on benzene also results in breakage of the ring. In other words, a pre-existing aryl-silicon bond appears to be required to avoid fragmentation.

Polymer Structure To examine the group of low intensity bands in the 1670 to 2000 cm^{-1} region of the infrared spectrum a thick polymer film (~ 25μm) was deposited on a silicon substrate at a temperature of 50°C from a phenylsilane plasma. This group of bands is frequently useful in identifying the substitution type of benzene rings[13]. The observed pattern agreed with what is expected for monosubstituted benzene rings.

A strong infrared band in the vicinity of 1370 cm^{-1} appears to be characteristic of benzene rings with two silicon substituents. We have observed it in disilylbenzene at 1370, in bis-(trichlorosilyl)-benzene at 1375, and in plasma polymers of disilylbenzene (prepared under a variety of conditions) at 1363 cm^{-1}. It is also found in the spectrum of p-bis-(trimethylsilyl)-benzene[14] at 1378 cm^{-1}.

In phenylsilane plasma polymers, however, no bands of significant intensity are seen in the 1400 to 1250 cm^{-1} region. The 1478 and 1100 cm^{-1} bands are characteristic of the monosilylbenzene structure[15]. The absence of the 1370 cm^{-1} band is taken as evidence against a substantial fraction of benzene rings possessing two silicon substituents.

It is therefore believed that phenylsilane plasma polymers contain benzene rings predominantly in monosubstituted form. This implies a structure of interconnected silicon chains with pendant phenyl groups.

Deposition Temperature and Cross-linking Although the rate of film growth decreases by nearly a factor of 30 when the substrate temperature is changed from 50 to 450°C, there is relatively little temperature dependence observed in the infrared spectrum. This is best seen from the absorption coefficients of the major bands plotted in Figure 2 as a function of substrate temperature.

The absorption coefficients, α, were calculated from the measured optical densities, O.D. = $\log_{10} I_0/I$, and from the film thickness, t, which is turn was computed from the spacings, s, of interference fringes appearing in the same infrared spectrum:

$$\alpha = \text{O.D.}/t = \text{O.D.} \times 2sn.$$

The refractive index, n, was assumed to be 1.8 for all the deposited films. For about half of the films, the thicknesses were also measured directly with a Tencor Alphastep profiler. In most instances the random error of ±10% in the thickness measurement was larger than systematic variations in n, justifying the assumption of constant n.

The only band whose intensity shows a strong dependence or preparation temperature, is the 2100 cm^{-1} silicon-hydrogen stretching mode. In view of analogous results in hydrogenated amorphous silicon deposited from SiH_4 plasmas[9] the loss of silicon-bound hydrogen at higher substrate temperatures is not surprising. As the loss of each pair of Si-H bonds corresponds to the formation of an Si-Si bond, the data imply that the cross link density of all arylsilane plasma polymer films prepared at a temperature higher than 50°C must be very high.

A similar substrate temperature dependence of the infrared intensities was observed in the plasma polymer films prepared from the other aromatic silanes. The only significant change in the 50° to 450°C range is the rapid decrease in the absorptions due to silicon-hydrogen bonds.

It is noteworthy that in diphenylsilane plasma polymer films there is a non-zero intensity of the Si-H stretch (at $T_s=250°C$ $\alpha_{2100}=22\pm5$ mm^{-1}). This indicates that it is not adequate to consider only the elimination of an H_2 molecule in every polymerization step. In some fraction of the cases, the incorporation of the monomer in the growing polymer chain must be combined instead with the breakage of a carbon-silicon bond.

Mixtures with Silane Films were deposited from an approximately equimolar mixture and also from SiH_4 containing 0.6 to 2.0 mole % phenylsilane. Infrared spectra in the first case were very similar to those of plasma polymers of pure phenylsilane. The carbon incorporated in the films obtained in the low phenylsilane concentration range, however, was conspicuously non-aromatic ($O.D._{2910}/O.D._{3040} \geq 3$).

4. DISCUSSION

The plasma chemistry of arylsilanes is clean in the sense that the important structural features of the starting material are preserved in the polymeric product. No significant ring fragmentation was observed, nor was any substitutional attack on the aromatic rings.

The main structural feature of the phenylsilane plasma polymers, as deduced from infrared spectroscopic evidence in the previous section, are summarized in Fig. 3. The stoichiometry requires that in the polymerization process each ΦSiH_3 molecule lose either an H_2 or a ΦH molecule, and further hydrogen is lost in the cross linking step. While the ratio of hydrogen to benzene elimination cannot be precisely quantified, infrared intensities indicate that H_2 loss is the major process and that the ratio in other arylsilanes is not very different from phenylsilane.

The polymerization mechanism remains the subject of speculation. The clean plasma chemistry implies that either (a) a rapidly condensing intermediate is formed upon electron impact from phenylsilane preferentially over fragmentation products common to other aromatic compounds, or (b) some chain propagating intermediate reacts rapidly with unexcited ΦSiH_3 molecules. The first alternative can be rationalized as a protective effect of the silyl group on the aromatic ring. That is excess vibrational energy, which in other aromatic molecules results in ring fragmentation, is rapidly dissipated in arylsilanes in the breakage of weak Si-H bonds. This, however leaves open the question as to why such stabilization is absent when the excess energy is provided by the attack of SiH_4 fragmentation products (rather than electron impact) as in the case of mixtures. Alternative (b) can be rationalized on the basis of bond energies[16]: in contrast to an analogous reaction in hydrocarbons, the formation of an Si-Si bond with the elimination of H_2 is exothermic. This alternative is compatible with the observations in the silane- phenylsilane mixtures if it is assumed that the chain propagating species is not an important product of the silane fragmentation.

Clean plasma chemistry, as is observed with pure arylsilanes, is unusual. It is also important as it implies that properties of the plasma polymer may be controlled by the proper choice of substituted arylsilane precursors.

ACKNOWLEDGEMENTS

I thank T.P. Fryxell for technical assistance, and J.A. Cutro for data on silane-phenylsilane mixtures.

REFERENCES

(1) (a) M. Millard, in "Techniques and Applications of Plasma Chemistry", J.R. Hollahan and A.T. Bell, editors, John Wiley and Sons, New York (1974), Chapter 5. (b) H. Hiratsuka, G. Akovali, M. Shen, and A.T. Bell, *J. Appl. Polymer Sci.* 22, 917 (1978) and references contained therein.

(2) K. Jesch, J.E. Bloor and P.L. Kronick, *J. Polymer Sci.* 4, 1487 (1966).

(3) F.J. Vastola and J.P. Wightman, *J. Appl. Chem.* 14, 69 (1964).

(4) D.D. Neiswender, *Adv. Chem. Series* 80, 338 (1969).

(5) L.S. Tuzov, A.B. Gilman, A.N. Shchurov and V.M. Kolotyrkin, *Polymer Sci.* USSR 9, 2728 (1967).

(6) R.C. Chittick, J.H. Alexander and H.F. Sterling, *J. Electrochem Soc.* 116, 77 (1969).

(7) W.E. Spear, *Advances Phys.* 26, 811 (1977).

(8) H. Fritzsche, C.C. Tsai and P.P. Persans, *Sol. St. Technol.* 1978, [1], 55.

(9) M.H. Brodsky, M. Cardona and J.J. Cuomo, *Phy. Rev.* B16, 3556 (1977).

(10) I. Haller, submitted for publication.

(11) N. Bilow, J.L. Brady and C.L. Segal, *J. Org. Chem* 26, 929 (1961).

(12) L.J. Bellamy, "Infrared Spectra of Complex Molecules", 3-d Edition, Wiley, New York (1975) pp. 19-21, 75.

(13) N.B. Colthup, L.H. Daly and S.E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, N.Y. (1969) pp. 228-230.

(14) S. Dobos, A. Szabo and B. Zelei, *Spectrochim. Acta.* 32A, 1393 (1976).

(15) W.W. Simons, "Sadtler Handbook of Infrared Spectra", Sadtler Research Laboratory, Inc., Philadelphia, PA (1978) pp. 321-329.

(16) J.D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York (1970).

Table I. Intensity ratios of aliphatic to aromatic IR absorptions for plasma polymers from various precursors. Preparation temperature 250°C, p = 0.1 torr.

Precursor	$\frac{O.D._{2840}}{O.D._{3040}}$	$\frac{O.D._{2910}}{O.D._{3040}}$
ΦSiH_3	0.15	0.17
$\Phi(SiH_3)_2$	0.15	0.31
$Cl\text{-}\Phi SiH_3$	0.10	0.16
Φ_2SiH_2	0.17	0.27
ΦCH_3	1.9	3.4
C_6H_6	0.71	1.38
C_6H_6 + SiH_4 mixture	3.0	3.5

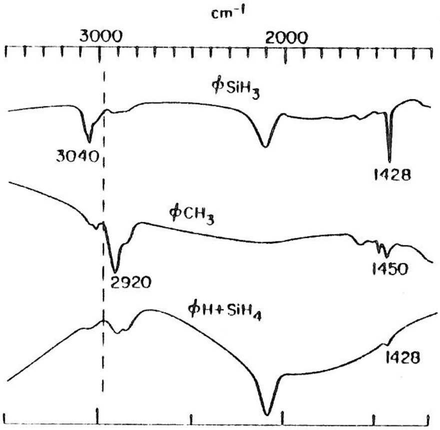

Fig. 1. Infrared spectra of plasma polymer films from the precursors indicated. Aromaticity is preserved only in the presence of Φ-Si bonds.

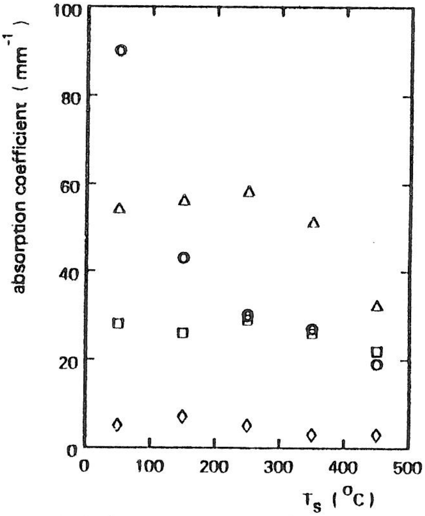

Fig. 2. Substrate temperature dependence of the absorption coefficients of various infrared bands of phenylsilane plasma polymers (α_{3010} -- squares; α_{2910} -- diamonds; α_{2100} -- circles; α_{1100} -- triangles).

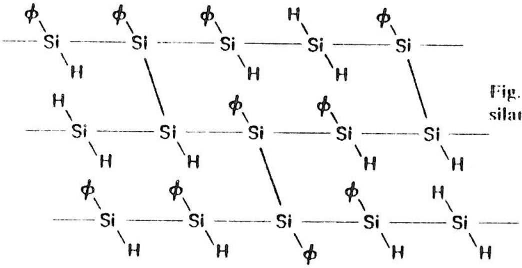

Fig. 3. Predominant structure of the phenylsilane plasma polymers.