ISPC-8 Tokyo, 1987
Paper number AVIII-02

GLOW DISCHARGE DECOMPOSITION OF PHENYLSILANE AND PROPERTIES OF DEPOSITED FILMS

T.Nakamura**, M.Funabashi, T.Hirano*, K.Fueki and H.Koinuma
Department of Industrial Chemistry/*Synthetic Chemistry
Faculty of Engineering, The University of Tokyo
Bunkyo-ku, Tokyo 113, Japan
**Technical Service and Development First Section,
Toray Silicone Co.,Ltd.
Ichihara-shi, Chiba 299-01, Japan

ABSTRACT

A series of studies has been carried out on the glow discharge decomposition of phenylsilane which was expected to deposit films with specific structures and electronic properties. Based on a semi-empirical molecular orbital calculation, the Si-C bond in phenylsilane was suggested to be stronger than the Si-C bond in methylsilane. However, carbon-containing ionic species were detected in the mass analysis of the phenylsilane plasma. In accordance with this plasma diagnosis, Si-phenyl bonds were scarcely preserved in the films deposited at high rf power conditions. A doping property of the films was also examined.

1. INTRODUCTION

Silanes with aromatic substituents are expected to show specific reactivities in plasma chemical reactions as well as to deposit films having specific electronic properties. Haller et al. reported phenyl-substituted silanes were polymerized without splitting off the benzene rings in an inductively coupled plasma to give crosslinked polysilane chains with the phenyl pendant groups1)-4). This result appears to be contrastive to the behavior of phenylsilane in a photo CVD where the phenyl group could easily be split off5).

In a previous study, we prepared amorphous silicon carbide(a-SiC) films by the glow discharge decomposition of methylsilanes and observed a qualitative correlation between the bond energies in the methylsilanes and the structure of deposited films; the strong Si-C bonds in methylsilanes were hardly decomposed by an ordinary rf power6).

In the present study, we have prepared amorphous films by the glow discharge decomposition of phenylsilane($SiH_3C_6H_5$) in order to investigate the decomposition profile of this compound in the plasma and to elucidate the structure and properties of the prepared films. The reaction mode was examined by a quantum chemical calculation on the electronic states of the starting material based on the MNDO(Modified Neglect of Diatomic Overlap) method and by the plasma diagnosis using a quadrupole mass spectrometer(QMS). Also investigated was the possibility of a chemical doping of the films by exposing them to iodine vapor, since the films, especially when the phenyl groups were largely preserved as in the case of phenylmethylpolysilane prepared by the polycondensation reaction7), should have properties somewhere between amorphous silicon and conjugated organic polymers.

2. EXPERIMENTAL

Phenylsilane was prepared by the hydrogenation of phenyltrichlorosilane and purified by the distillations(119°C at 1atm).

The molecular orbital(MO) calculations were conducted by the semi-empirical MNDO method using an M-680H computer system at The University of Tokyo.

The films were deposited in a capasitively coupled plasma CVD apparatus (13.56MHz, electrode 10cmϕ,3cm distance). As phenylsilane is liquid at room temperature, it was saturated in a carrier gas(helium) at a constant temperature. Then the mixed gas was introduced into the reactor at a flow rate of 10sccm(partial flow rate of phenylsilane:0.9sccm) and it was decomposed by the glow discharge under such conditions as follows. Total pressure:300-700mTorr, rf power:0.5-80W, substrate temperature:100°C. Both Corning #7059 glass and single-crystal silicon wafers were used as substrates.

Ionic species in the plasma were diagnosed by a Spectramass SELECTORR quadrupole mass spectrometer without using an ionizing filament. The thicknesses of films were measured by a Taylor Hobson TALYSTEP. The optical band gaps of films were determined from the intercepts of linear parts of$(\alpha h\nu)^{1/2}$ vs hν plots which were derived from UV-VIS spectra measured by a HITACHI-340 spectrometer. The structure of films was analyzed by a Shimadzu FTIR 4000 spectrometer. The electronic conductivities were measured by the gap-cell method.

A chemical doping were carried out on the films with evaporated gold electrodes by exposing the films to iodine vapor which was saturated in air at room temperature.

3. RESULTS

(1) Electronic States of Phenylsilane

Table I shows the results of the MNDO MO calculation on phenylsilane, together with that on methylsilane listed for comparison. The two center bond energies for the Si-H and the Si-C in phenylsilane are stronger than the correspon-

Table I. Two center bond energies, frontier orbital energies and total energies calculated by MNDO method.

Molecule	Bond Energy (eV)				Orbital Energy (eV)		
	Si-H	Si-C	C-H	C-C	HOMO	LUMO	ΔE_O
SiH_3CH_3	-9.96	-13.09	-12.32		-11.90	0.24	12.14
$SiH_3C_6H_5$	12.68	-16.30	-12.90	-20.01	-9.38	0.17	9.55

	Total Energy (eV)		
	Ground State	Lowest Excited Triplet State	ΔE_T
SiH_3CH_3	-308.8	-296.1	12.7
$SiH_3C_6H_5$	-967.8	-964.8	3.0

ding energies in methylsilane. The difference between the HOMO (Highest Occupied Molecular Orbital) and LUMO(Lowest Unoccupied Molecular Orbital) energies, ΔE_O, for phenylsilane is relatively smaller than ΔE_O for methylsilane. The difference of the total energies between the ground state and the lowest excited triplet state, ΔE_T, for phenylsilane is much smaller than ΔE_T for methylsilane.

(2) Plasma Diagnosis

In the QMS analysis of phenylsilane plasma, four main ionic species, mass numbers of 15, 26, 78 and 107 were detected. These species were assigned to CH_3^+, $C_2H_2^+$, $C_6H_6^+$ and $SiH_2C_6H_5^+$, respectively. Figure 1 shows the dependence of the partial pressures of these four ionic species on the rf power for the plasma of 300mTorr total pressure. At total pressures of 500mTorr and 700mTorr, almost the same results as these shown in Figure 1 were obtained. In the power range below 5W, the partial pressures of the ions were too small to be detected. The partial pressures of methyl and acetylene ions clearly increased as the rf power increased. On the contrary, benzene and phenylsilyl ions were present at relatively high levels even in lower rf power range($\lesssim$10W) and their concentrations were not so sensitive to the rf power. These results suggest that the hydrogen and phenyl group are easily cleaved from phenylsilane and that the further decomposition of the split phenyl radical is promoted by the increase of rf power.

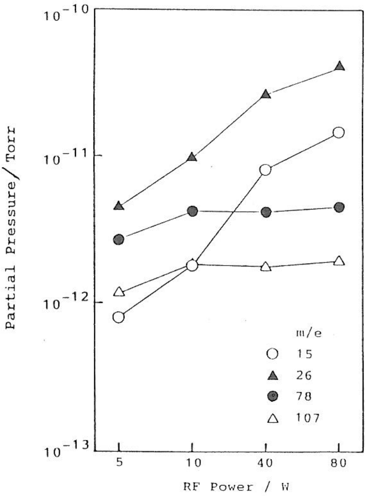

Fig.1. Dependences of the partial pressures of main ionic species in the phenyl silane plasma on the rf power (ionizing filament; off, total pressure = 300mTorr).

(3) Deposition Rate

Figure 2 shows the dependences of the film deposition rates on the rf power in the plasmas of various total pressures. The deposition rate decreases as the rf power increases. The films deposited at relatively high rf powers were very hard and had dark brown colors, whereas

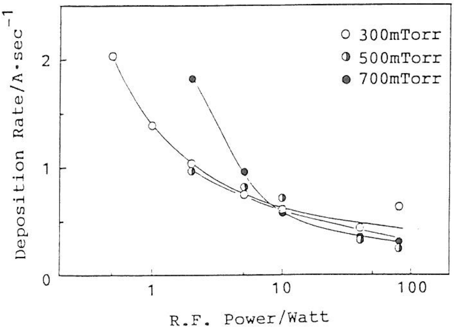

Fig.2. Dependences of the deposition rates of amorphous films from phenylsilane at the total pressures of 300, 500 and 700mTorr on the rf power.

those deposited at lower rf powers were apparently softer and almost colorless. The decreased deposition rates at high rf power conditions may be originated from the enhanced decomposition of phenylsilane in the gas phase into relatively lower concentration of Si-containing fragments and higher concentration of C-containing fragments as the film precursors, since the total pressure is kept constant. The sticking coefficients of C-containing species were reported to be lower than those of Si-containing species[8).

(4) Structure and Properties of Films

In the IR spectra of the deposited films, absorptions due to C-H and Si-H stretchings could be clearly seen at 2800 - 3100cm^{-1} and 2100 - 2200cm^{-1}, respectively. Absorptions at about 1430cm^{-1} which were observed in the films prepared at lower rf powers($\leq$2W) can be assigned to C-C stretchings in phenyl rings. Figure 3 shows the FT-IR spectra of the films. The absorption intensity at 3050cm^{-1}, which can be assigned to the C-H bond in aromatic groups, is higher in the films prepared at lower rf powers. In the film prepared at an rf power of 0.5W, the intensity for the aromatic C-H bonds is larger than that at 2900cm^{-1} for the aliphatic C-H bonds. The intensity of the absorption due to Si-H bond decreased when the film was deposited at increasing rf power.

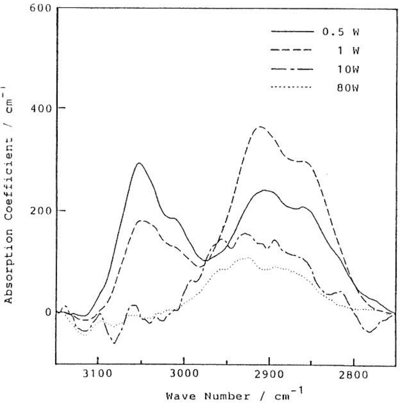

Fig.3. IR spectra of amorphous films prepared from phenylsilane at the rf powers of 0.5, 1, 10 and 80W (total pressure = 300mTorr).

Figure 4 shows the dependences of the optical band gaps(E_{opt}) of the films on the rf powers used for the film depositions: the E_{opt} decrease with increasing rf power applied for the film preparation.

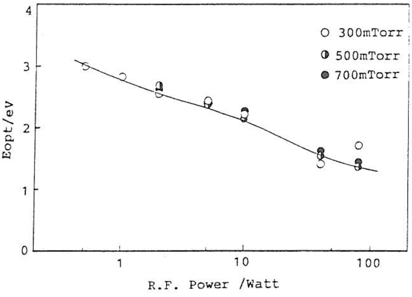

Fig.4. Optical band gaps of amorphous films prepared from phenylsilane at the total pressures of 300, 500 and 700mTorr as a function of the rf power.

According to the IR spectra and the E_{opt} data, it is concluded that the films prepared at low rf powers (<10W) have higher contents of phenyl and Si-H gruops. The Si-C bond and the benzene ring in phenylsilane were presumed not to be decomposed so much by such a low rf power and precursors containing Si-Ph structure could be incorporated in the film. The large E_{opt} of ca. 3eV (much larger than 1.7eV in a-Si:H) is probably due to the phenyl groups and polymeric (or so-called "pseudo one-dimentional" polysilane) structure. In contrast, the films prepared at high rf powers(≥10W) have less content of phenyl groups and small total hydrogen contents (including C-H and Si-H bonds). Judging from the IR spectra, the dark brown colors and the E_{opt} values(1.5-2.0eV), the films should have mixed structures of graphitelike clustered carbon and a-SiC.

Both the dark and photo conductivities of all the as-deposited films were in the range of 10^{-10}-10^{-12} $S\cdot cm^{-1}$. Figure 5 shows the conductivity variation by an exposure of the films to iodine(I_2) vapor. All the samples tested showed conductivity enhancements to as high as $10^{-7}S\cdot cm^{-1}$. The conductivities dropped a little by the light irradiation from a Xe lamp, probably due to the partial evaporation of iodine absorbed in the films. Thus, the chemical doping effect was clearly observed in the amorphous films prepared from phenylsilane.

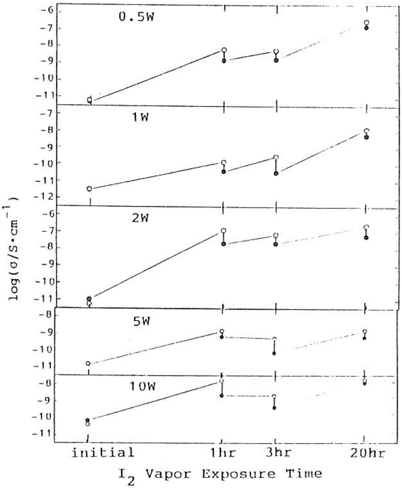

Fig.5. Conductivities of amorphous films prepared from phenylsilane at the rf powers of 0.5, 1, 2,5 and 10W (total pressure = 300mTorr) exposed to the vapor of iodine saturated in air at room temperature
(○ ; dark conductivity
● ; photo(Xe lamp) conductivity)

4. DISCUSSION

The decomposition profile in phenylsilane was found to be contrastive to that in methylsilane. The facile cleavage of the Si-C bond in phenylsilane and not in methylsilane can hardly be explained only by the two center bond energies of the Si-C's. The following two explanations are plausible.

1) Judging from the ΔE_O and ΔE_T values, phenylsilane is far easily excited to the triplet state than methylsilane and the decomposition of phenylsilane to give film precursors occurs from the triplet excited state.

2) Also calculated were total energies as a function of the bond length of the Si-C in both phenylsilane and methylsilane. Although the energy minimum for methylsilane is quite deep at the optimized position, that for phenylsilane is rather shallow. Therefore, the Si-C bond in phenylsilane can easily be stretched long enough to be split off than that in methylsilane.

5. CONCLUSION

The glow discharge decomposition of phenylsilane was found to be strongly dependent on the rf power. According to the plasma diagnosis by QMS, the elimination and decomposition of the phenyl group was promoted as the rf power increased. Explanations based on a quantum chemical calculation were attempted for this decomposition profile. The structures of the films prepared at low rf powers contained higher amounts of phenyl groups and had E_{opt} of ca. 3eV. The films prepared at high rf powers had lower hydrogen contents and E_{opt} values of 1.5-2.0eV. The films could be chemically doped by exposing them to iodine vapor.

REFERENCES

1) I.Haller, Symp.Proc.-Int.Symp.Plasma Chem.,5th,**1**,249(1981)
2) I.Haller, J.Electrochem.Soc.,**129**,180(1982)
3) P.Oelhafen,J.A.Cutro and I.Haller, J.Electron Spectrosc.Relat. Phenom.,**34**,105(1984)
4) J.A.Cutro and I.Haller, Mater.Res.Soc.Symp.Proc.,38(Plasma Synth.Etching Electron.Mater.),343(1985)
5) T.Tomoda,H.Fujioka,M.Inoue and Y.Tanaka, Extended Abstracts (The 33rd Spring Meeting,1986);Jpn.Soc.Appl.Phys.& Relat.Soc., 4p-ZD-13
6) H.Koinuma,M.Funabashi,K.Kishio,M.Kawasaki,T.Hirano and K.Fueki Jpn.J.Appl.Phys.,**25**,1811(1986)
7) R.West,L.D.David,P.I.Djurovich,K.L.Stearley,K.S.V.Srinivasan and H.Yu, J.Am.Chem.Soc.,**103**,7352(1981)
8) K.Tachibana,H.Harima and Y.Urano, Extended Abstracts(The 47th Autumn Meeting,1986);Jpn.Soc.Appl.Phys.,28p-Z-11