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## Effect of Glow Discharge Conditions on Structure and Thermal Properties of Polysilazane Thin Films

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### ABSTRACT

Polysilazane thin films were prepared by glow discharge polymerization of hexamethylcyclotrisilazane in mixture with various gases: argon, nitrogen, hydrogen and ammonia. The effect of gas type on thermal stability and chemical structure of glow discharge polysilazane was studied. Thermogravimetric measurements performed within a temperature range of 20-1000°C, showed that the best thermal stability was exhibited by polysilazane prepared at the presence of ammonia in the reaction mixture. IR analyses data revealed that polymers prepared from mixture with ammonia or hydrogen contained more Si-H groups than those obtained with argon or nitrogen. It proves that in the presence of ammonia or hydrogen, greater monomer fragmentation through Si-C bonds cleavage takes place. More detailed investigations were carried out for polysilazanes prepared in mixture with ammonia. It was found that thermal stability as well as chemical structure of polymer depend strongly on polymerization conditions, i. e., ammonia contents in the reaction mixture, deposition time, discharge current density. Thermal stability of polysilazane improved with the increase in deposition time and current density. Increasing

these parameters caused also the Si-NH-Si bonds content in the polymer to grow. The results prove that ammonia is a reactive comonomer and that the polymerization of hexamethylcyclotrisilazane at the presence of this gas may proceed through the formation of Si-NH-Si bonds.

## INTRODUCTION

Of the numerous thin polymer films prepared by glow discharge polymerization in various monomers, the polyorganosilicon films have many properties of particularly great interest. The films, due to their high thermal stability [1], high dielectric strength [1-3], and outstanding optical properties [3-5], may be used in modern technology as coatings of various type. Most of the published papers concern studies of thin polymer films prepared from organosiloxane monomers. Considering the properties of organosilicon monomers we found a possibility to prepare polymer films of considerable higher thermal stability than of polysiloxane films from organosilazane compounds. It is worthy of note that conventional polysilazanes show good thermal stability at temperatures up to 500°C, while polysiloxanes decompose at a temperature of 350°C [6]. Our examination of the properties of polysilazane thin films prepared by glow discharge polymerization of hexamethylcyclotrisilazane has shown that the films have outstanding thermal stability and adhesion to metallic substrates [7].

The present paper contains results of studies on the effect of various gases present in the mixture with the hexamethylcyclotrisilazane vapor on the chemical structure and thermal stability of polysilazane thin films.

## EXPERIMENTAL

Glow discharge polymerizations were carried out in the electrode static system. Details of the apparatus used for this study have been reported previously [8]. Polysilazane films were deposited during glow discharge operating at 20 kHz on the surface of two parallel stainless steel electrodes with the electrode gap fixed at 3 cm.

Thermogravimetric analyses (TGA) of the polymer samples were carried out within the temperature range 20-1000°C by using a Perkin-Elmer Model TGS1 thermobalance. A polymer sample of ca. 4 mg was heated at a constant rate of 8°C/min in nitrogen atmosphere. Nitrogen flow rate through thermobalance was 30 cm<sup>3</sup>/min.

Infrared spectra of polymer films were recorded on a Perkin-Elmer, Model 457, spectrophotometer using ATR technique.

The surface of electrodes was cleaned by glow discharge in argon during 5 min prior to polymer film deposition and its purity was tested using ATR infrared analysis.

Hexamethylcyclotrisilazane, PCR product, was purified by rectification with a Perkin-Elmer Model 151, column with Teflon spinning band, and the purity was tested by gas chromatography.

## RESULTS AND DISCUSSION

### Effect of Gas Type in Mixture with Monomer Vapor

In order to study the effect of various gases in mixture with monomer vapor on chemical structure and thermal stability of polymer film, glow discharge polymerization of hexamethylcyclotrisilazane was carried out in the presence of such gases as ammonia, hydrogen, nitrogen, and argon. The discharges were made at the same partial pressures of monomer and gas equal to 0.3 Torr and at a current density  $j = 1 \text{ mA/cm}^2$  for  $t = 20 \text{ sec}$ .

On evaluating the surface and properties of the films prepared it was found that the presence of ammonia in the reaction mixture promoted the formation of transparent, colorless polymer film of extremely high adhesion to metallic substrate with no powder products which are often observed during a glow discharge polymerization. In the presence of hydrogen there was formed a film containing small powder regions. The films prepared with the addition of ammonia and hydrogen were resistant to the action of such organic solvents as acetone, benzene, and n-heptane. Nitrogen or argon addition to the monomer vapor brought about a considerable deterioration of the film adhesion to substrate. The films prepared in the presence of these gases includes large regions of powder and underwent swelling in organic solvents.

The IR analysis showed that absorption spectra of polysilazane films prepared with various gases are much the same and the only differences were quantitative changes in some absorption bands (Fig. 1). The spectra exhibited strong absorption bands at 3400, 1170, and  $900 \text{ cm}^{-1}$  (Fig. 1a) which arise from Si-NH-Si system and correspond to vibrations  $\nu(\text{NH})$ ,  $\delta(\text{NH})$  and  $\nu_{\text{as}}(\text{SiNSi})$ , respectively.

The presence of Si-CH<sub>3</sub> groups in the polymer is demonstrated by a strong and sharp absorption band at  $1250 \text{ cm}^{-1}$  arising from the  $\nu_{\text{s}}(\text{CH}_3)$  vibration as well as by the absorption at  $790 \text{ cm}^{-1}$  corresponding to  $\nu(\text{SiC})$  and  $\rho(\text{CH}_3)$  vibrations. The spectra of polysilazane

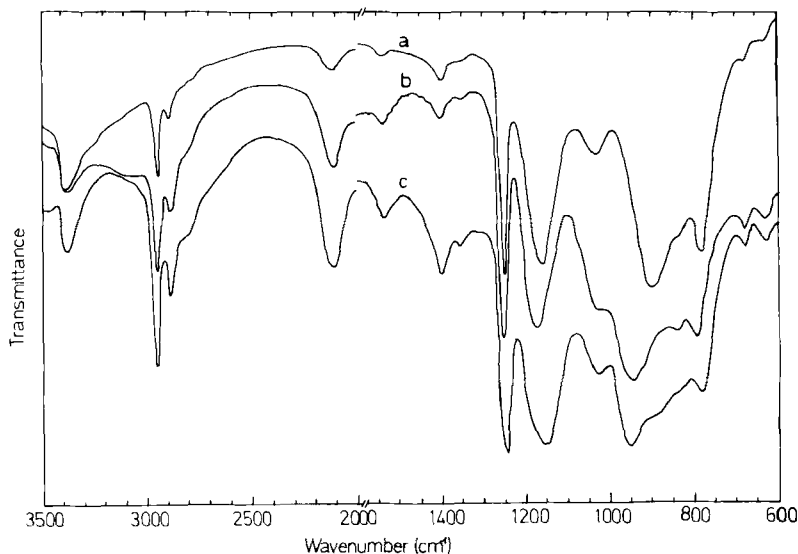


FIG. 1. ATR infrared spectra of polysilazane films deposited from monomer-ammonia mixture ( $P_M = 0.3$  Torr,  $P_{NH_3} = 0.9$  Torr) at various glow discharge parameters: (a)  $t = 20$  sec,  $j = 1$  mA/cm<sup>2</sup>; (b)  $t = 20$  sec,  $j = 2$  mA/cm<sup>2</sup>; (c)  $t = 60$  sec,  $j = 1$  mA/cm<sup>2</sup>.

films exhibited new absorption bands at 2120 and 1030 cm<sup>-1</sup> which are absent in the monomer spectrum. The former at 2120 cm<sup>-1</sup> corresponds to the  $\nu(\text{SiH})$  vibration. These groups may be formed by fragmentation of the monomer molecules leading to the cleavage of Si-C bonds [9]. The absorption band at 1030 cm<sup>-1</sup> is a typical one for methylene groups situated between two silicon atoms and corresponds to vibration  $\omega(\text{CH}_2)$ . The presence of these bonds in the polymer structure is confirmed by a weak but distinct band at 1350 cm<sup>-1</sup> characteristic of the  $\nu_s(\text{SiCH}_2\text{Si})$  vibration [10].

Quantitative analysis of IR spectra of polymer films prepared at the presence of various gases in mixture with monomer exhibited a change in the relative intensity of absorption bands at 2120 cm<sup>-1</sup> and 1250 cm<sup>-1</sup> corresponding to vibration of SiH and SiCH<sub>3</sub>, respectively. The ratio of areas under the absorption peaks  $A_{\text{SiH}}/A_{\text{SiCH}_3}$  corresponds to SiH groups content in the polymer structure and characterizes to some extent, monomer fragmentation connected with splitting off methyl groups from silicon. It is seen from Table 1

TABLE 1. Relative IR Absorption Intensity,  $A_{\text{SiH}}/A_{\text{SiCH}_3}$ , and Relative Pressure Increase,  $\Delta p/p_0$ , for Presence of Various Types of Gas in Mixture with Hexamethylcyclotrisilazane Vapor

Gas admixed	$A_{\text{SiH}}/A_{\text{SiCH}_3}$	$\Delta p/p_0$ (%)
Ammonia	0.36	12
Hydrogen	0.32	10
Nitrogen	0.24	7
Argon	0.22	6

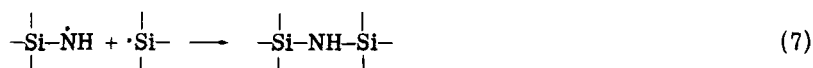
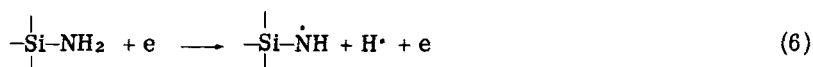
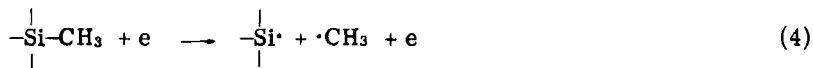
that the values of that ratio are the highest for films prepared in the presence of ammonia or hydrogen. It may be then, concluded that the degree of fragmentation of monomer molecules in the presence of ammonia or hydrogen in the reaction mixture is higher than that in the presence of nitrogen and argon. The results agree with the measurements of relative increase in pressure ( $\Delta p/p_0$ ) in the reac-

tion system during the glow discharge. The highest increases in pressure were observed during discharge in the presence of ammonia and hydrogen (Table 1). These gases, due to their lower dissociation energies ( $\text{NH}_3$ , 4.8 eV;  $\text{H}_2$ , 4.5 eV) relative to nitrogen (9.8 eV) [12], dissociate more easily under the glow discharge conditions with formation of atomic hydrogen which causes the strong fragmentation of the monomer molecules. These phenomena find their confirmation in higher SiH group content in the polymer as observed in the presence of ammonia or hydrogen.

To examine the fragmentation of the gases, discharges in mixtures of particular gas with argon were carried out at the same discharge conditions as in polymerization. Relative increases in pressure for ammonia and hydrogen were 3 and 2%, respectively. There was no observable pressure increase during discharge in the nitrogen-argon mixture and in pure argon. The results suggest that ammonia may undergo dissociation during discharge, resulting in the formation of amine and imine radicals as well as atomic hydrogen. This process may take place according to the scheme shown in Eqs. (1)-(3).



According to the literature data [11], the dissociation of ammonia proceeds mostly in accordance with reaction (1). Owing to the high reactivity of amine radicals formed by the ammonia dissociation, the polymerization of hexamethylcyclotrisilazane in the presence of ammonia may lead to crosslinking of the polymer according to the mechanism shown in Eqs. (4)-(7).



It follows from the thermogravimetric measurements that the thermal stability of the glow discharge polysilazane depends closely on the type of gas present in the mixture with monomer vapor during discharge. It is seen from the shape of TG curves in Fig. 2 that the thermal decomposition of polysilazane proceeds through several stages. At the first stage up to about 250°C a sharp inflection in all the curves is observed which is connected with a rapid weight loss [1 - (w/w<sub>0</sub>)]. This is due to the evolution of low molecular products trapped in the polymer structure during polymerization. Our earlier gas chromatography and mass spectrometry studies have shown that the glow discharge polysilazane contains a small amount of low molecular products such as monomer, octamethylcyclotetrasilazane, and dicyclic dimer [13]. As is seen from Fig. 2, at the first stage of decomposition the lowest weight loss is in the polymer obtained in the presence of ammonia. This would suggest that the polymer contains the smallest amount of low molecular products. Further course of the TG curves shows that at 800°C the rate of decomposition reaches zero for all the polymer samples under investigation. The highest weight of residue (w/w<sub>0</sub>) at this temperature is observed in the case polymers prepared in the presence of hydrogen and ammonia. Hence, a conclusion may be drawn that the polymer films prepared in the presence of those gases exhibit considerable contents of highly crosslinked inorganic structures due to the strong fragmentation previously found.

To study the reactivity of ammonia under the glow discharge

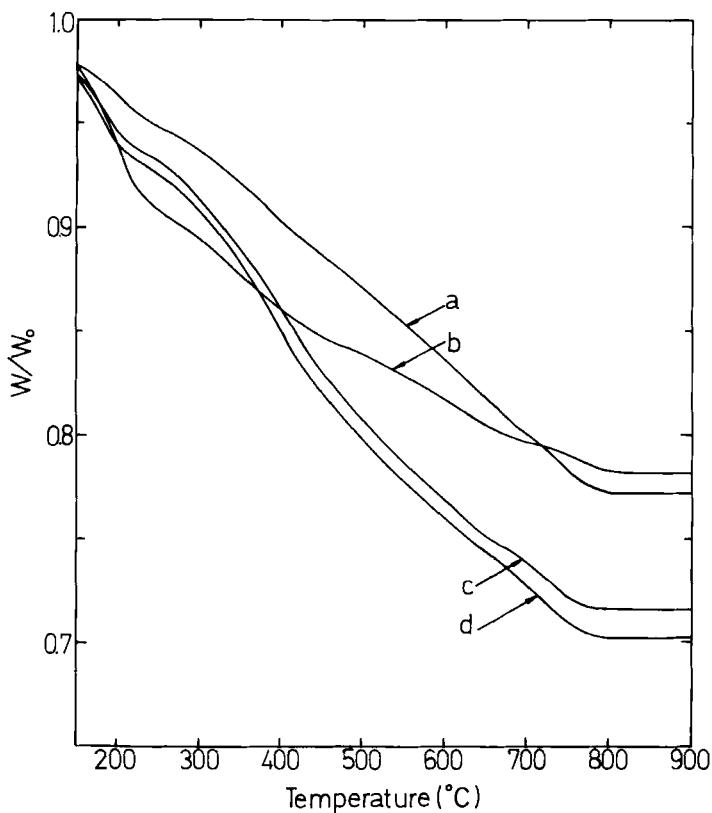


FIG. 2. Thermograms of polysilazanes deposited with content of various gas type in mixture with monomer vapor: (a) M + NH<sub>3</sub>; (b) M + H<sub>2</sub>; (c) M + N<sub>2</sub>; (d) M + Ar. Glow discharge conditions:  $P_M = P_{Gas} = 0.3$  Torr,  $t = 20$  sec;  $j = 1$  mA/cm<sup>2</sup>.

conditions, polymerizations of hexamethyldisiloxane (HMDS) were carried out in the systems: HMDS-argon and HMDS-ammonia under the same conditions as in previous experiments. It is clear from Fig. 3 that the IR spectrum of the polymer film prepared in the presence of ammonia (Fig. 3b) has additional distinct absorption bands at 1170 and 930 cm<sup>-1</sup> as compared to the spectrum of the polymer prepared in the presence of argon (Fig. 3a).

These absorption bands, as was previously described, are characteristic of the vibration of the Si-NH-Si system. In the spectrum of the polymer film prepared in the presence of ammonia at higher



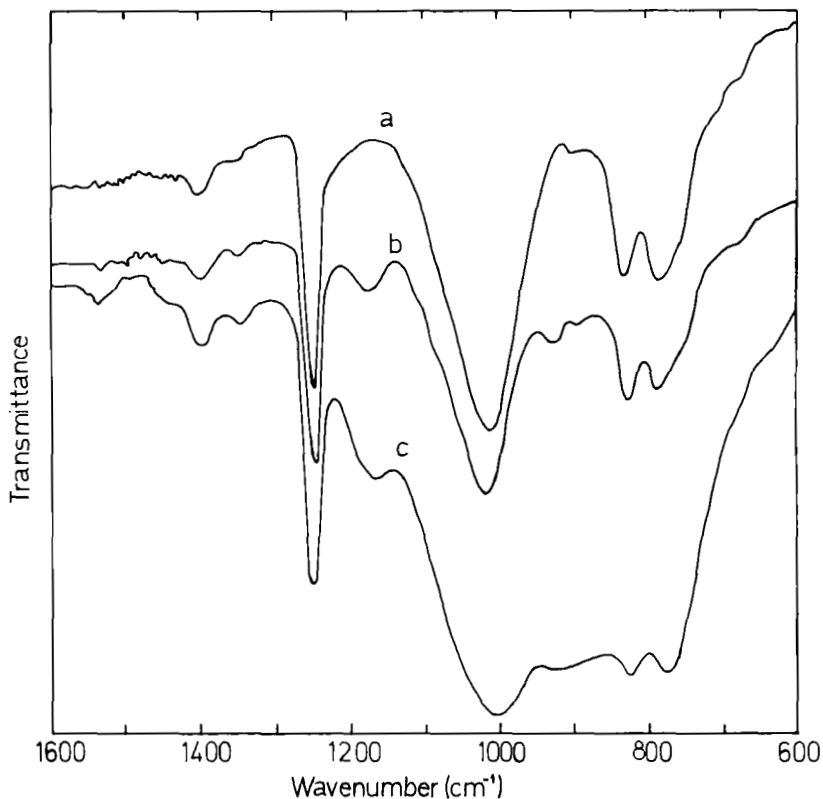


FIG. 3. ATR infrared spectra of polysiloxane films deposited from mixture of hexamethyldisiloxane vapor with argon or ammonia at  $P_M = P_{Gas} = 0.3$  Torr: (a) HMDS-argon,  $j = 1$  mA/cm<sup>2</sup>; (b) HMDS-ammonia,  $j = 1$  mA/cm<sup>2</sup>; (c) HMDS-ammonia,  $j = 2$  mA/cm<sup>2</sup>.

current density equal to 2 mA cm<sup>2</sup> (Fig. 3c) there is seen a clear increase in absorption at the same wavenumbers and appears a new band at 1540 cm<sup>-1</sup> which comes from the Si-NH<sub>2</sub> groups.

These results prove that ammonia under glow discharge conditions is a reactive comonomer and that polymerization with an addition of this gas involves crosslinking through splitting off methyl groups from silicon, resulting in the formation of Si-NH-Si bonds of a high thermal stability.

This corresponds to our findings which show the highest degree of monomer fragmentation in the presence of this gas and considerable increase in thermal stability of polysilazane film.

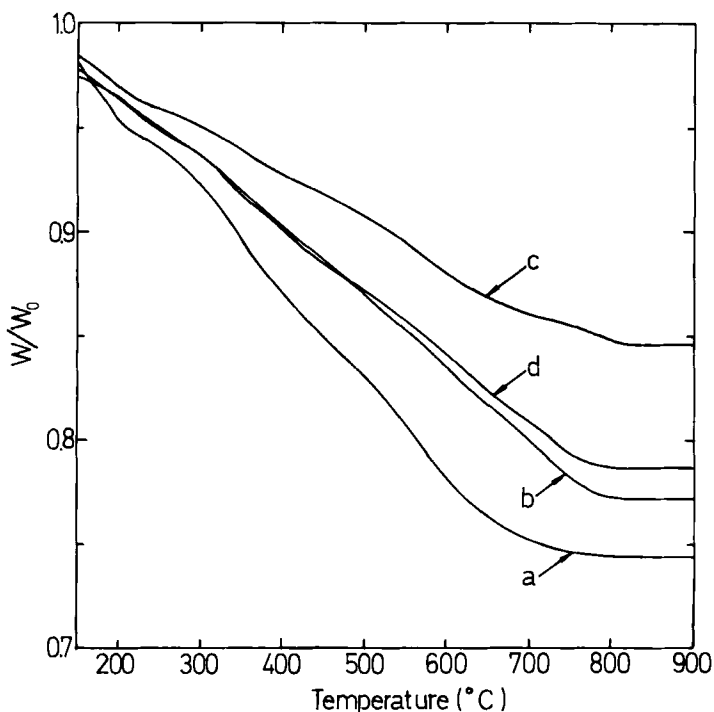


FIG. 4. Thermograms of polysilazanes deposited with various ammonia content in mixture with monomer vapor: (a) without ammonia; (b)  $P_{NH_3} = 0.3$  Torr; (c)  $P_{NH_3} = 0.6$  Torr; (d)  $P_{NH_3} = 0.9$  Torr. Glow discharge conditions:  $P_M = 0.3$  Torr,  $t = 20$  sec,  $j = 1$  mA/cm<sup>2</sup>.

On taking into account the high thermal stability of polysilazane films prepared at the presence of ammonia and their extremely strong adhesion to metallic substrate, more detailed investigations were carried out for these polymers.

#### Effect of Ammonia Contents and Discharge Parameters

To examine the effect of ammonia contents in mixture with monomer vapor on the thermal stability of the glow discharge polysilazane, thermograms were made from polymers prepared at various partial pressures of ammonia within the range  $P_{NH_3} = 0-0.9$  Torr, with the

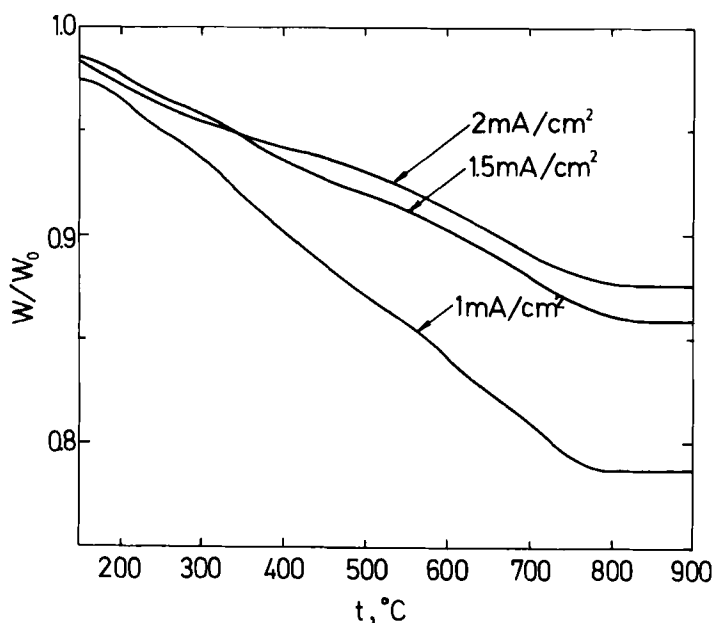


FIG. 5. Thermograms of polysilazanes deposited from monomer-ammonia mixture at various discharge current densities. Glow discharge parameters:  $P_M = 0.3$  Torr,  $P_{\text{NH}_3} = 0.9$  Torr;  $t = 20$  sec.

partial pressure of monomer being  $P_M = 0.3$  Torr and the rest of parameters as in previous experiments. It follows from the thermograms in Fig. 4 that the increasing of ammonia partial pressure in the mixture with monomer vapor within the range 0–0.6 Torr is accompanied by an improvement of the thermal stability of the polymer. With an increase in the ammonia content there is an increase of thermostable Si–NH–Si bonds in the polymer structure according to the mechanism previously proposed. Higher weight loss as observed in the TG curve for  $P_{\text{NH}_3} = 0.9$  Torr (Fig. 4d) may be caused by lower degree of crosslinking of the polymer, resulting from the considerably increased pressure in the reaction system.

In order to investigate the effect of the glow discharge parameters on the thermal stability of polysilazane, thermogravimetric analysis was carried out for the polymers prepared in the presence of ammonia at  $P_{\text{NH}_3} = 0.9$  Torr and at various current densities and deposition times. The slopes of TG curves in Figs. 5 and 6 show that the rate of weight loss decreases with the increase both in current density

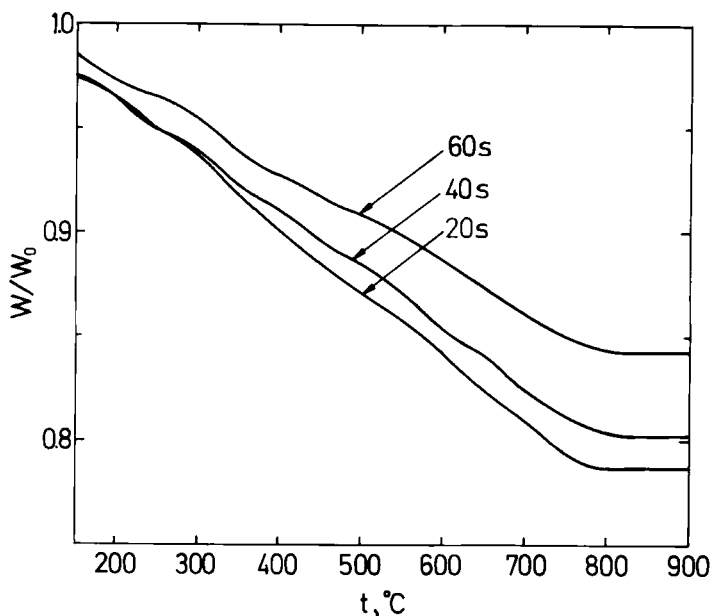


FIG. 6. Thermograms of polysilazanes deposited from monomer-ammonia mixture at various deposition times. Glow discharge parameters:  $P_M = 0.3$  Torr,  $P_{NH_3} = 0.9$  Torr;  $j = 1$  mA/cm<sup>2</sup>.

(Fig. 5) and deposition time (Fig. 6). Low weight loss observed at higher current densities and after longer deposition times would prove that the raise of the mentioned parameters is accompanied by the increase in the fragmentation of monomer which forms a highly crosslinked polymer films through the reaction with ammonia. The results are in agreement with our previous studies which have proved that with the increase in current density there was a decrease in the methyl group content in the polymer structure [9].

The IR analysis of polysilazane films prepared in the presence of ammonia under various discharge conditions exhibited quantitative changes in some absorption bands. As is seen from the spectra shown in Fig. 1, the increases in current density (Fig. 1a and 1b) and in deposition time (Fig. 1a and 1c) are accompanied by a distinct rise in absorption at 2120 and 1540 cm<sup>-1</sup> corresponding to vibrations of the SiH and SiNH<sub>2</sub> groups, respectively. The increase in these groups in the polymer is due to the strong fragmentation of monomer at the presence of ammonia. An increase in absorption is also observed at 1350 and 1030 cm<sup>-1</sup> which is characteristic for the Si-(CH<sub>2</sub>)<sub>1</sub> or 2<sup>-</sup>Si

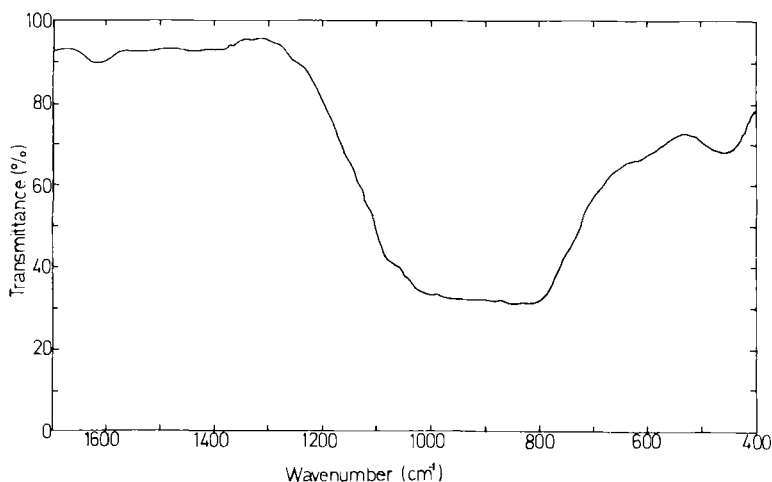


FIG. 7. ATR infrared spectrum of polysilazane film after heat treatment in vacuo ( $10^{-5}$  Torr) at  $800^{\circ}\text{C}$ .

system. The presence of these bonds suggests a possibility of polymer crosslinking through formation of methylene and ethylene bridges between silicon atoms. As is seen from Fig. 1 the absorption band for vibration  $\nu_{\text{as}}(\text{SiNSi})$  at  $900\text{ cm}^{-1}$  (Fig. 1a) shifts to  $950\text{ cm}^{-1}$  (Fig. 1b and 1c) with the increases in current density and in deposition time. The shifts of this absorption band towards higher wavenumber may result from the polymer crosslinking through the elimination of the hydrogen atom from the  $-\text{NH}-$  group and formation of bonds with tertiary nitrogen:  $(\equiv\text{Si})_3\text{N}$  [14]. The results are in agreement with the TGA data which have shown a high degree of polymer crosslinking.

### Thermal Modification of Thin Films

The high thermal stability of polysilazane films and, as follows from the thermograms, relatively low contents of organic structure in the polymer, suggested that these films may be changed into films of almost all inorganic structure and of higher thermal stability by a suitable thermal modification. Our studies on polysilazane films modified in vacuo at elevated temperature confirmed that such a treatment eliminates all the organic groups from the polymer and forms a glassy film of strong adhesion to metallic substrate [15].

The IR spectrum of thermally modified polysilazane film in (Fig. 7) shows a strong and broad absorption band in the range 1000-800  $\text{cm}^{-1}$ . It should be noted that a similar absorption band is present in the spectrum of silicon nitride [16]. Hence, one may conclude that thermally modified film has a silicon-nitrogen inorganic structure.

### CONCLUSIONS

The chemical structure, properties, and thermal stability of polysilazane film are closely dependent on the type of gas present in the mixture with monomer. The addition of ammonia causes the Si-NH-Si bonds to increase in the polymer structure and considerably improves the thermal stability of the polymer film and its adhesion to metallic substrate.

The thermal stability of the film depends closely on the glow discharge parameters and is improved with increasing current density and deposition time.

Thermal modification of polysilazane film gradually eliminates the organic structure from the polymer and gives rise to formation of an inorganic coating of high thermal resistance and strong adhesion to metallic substrate.

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