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## **Aging Process in Plasma-Polymerized Organosilicon Thin Films**

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### **ABSTRACT**

The atmospheric aging process in plasma-polymerized organosilicon thin films was studied. The investigations were carried out for plasma polymers produced from methylsilane, methylsilazane, and methylsiloxane, structurally different monomers. ATR-IR spectroscopic examinations revealed the strong effect of aging on the films structure. The formation of  $-OH$ ,  $>C=O$ ,  $Si-O-Si$ , and  $Si-O-C$  groups and the decay of  $SiH$  groups were found to be general trends in the structural changes of the plasma polymers investigated that resulted from aging. Mechanisms of the reactions contributing to the aging process were discussed. Kinetic studies indicated that the aging process is controlled by the diffusion of atmospheric oxygen and water into the film. Wettability data showed that aging produces distinct changes in the surface energy components of the films, increasing the dispersion component and decreasing the polar component. This trend was consistent with the structural changes observed for aged films.

## INTRODUCTION

Of the numerous organic polymer films which have been obtained by using the plasma polymerization technique, those produced from the organosilicones were found to have rather unique properties, promising for various practical applications. Plasma-polymerized organosilicon thin films, owing to their excellent thermal [1-4] and chemical [2, 5] resistance and their outstanding electrical [6, 7], optical [8, 9], and biomedical [10] properties, may find use in many branches of modern technology; for example, as protective coatings and encapsulants, as dielectrics in microelectronics, as antireflection coatings in conventional optics, as thin film light guides in integrated optics, and as highly biocompatible materials in medicine.

However, due to their specific nature resulting from the relatively high concentration of trapped free radicals, plasma-polymerized materials are strongly susceptible to reaction with air [11]. In many of the potential applications of these materials, a knowledge of their behavior in the atmosphere is of particular importance. Therefore, the present studies were undertaken to estimate the effect of atmospheric aging on the structure and some surface properties of plasma polymer films produced from such organosilicon monomers as methylsilanes, methylsilazanes, and methylsiloxanes of linear and cyclic structure. The mechanism of the aging process was also considered.

## EXPERIMENTAL

### Plasma Polymerization Procedure

The plasma polymerization process was carried out in an audio frequency glow discharge operated at 20 kHz using the electrode system described in detail elsewhere [12]. Polymer films were deposited onto polished surface of stainless steel electrodes, each of 50 cm<sup>2</sup> surface area, spaced 3 cm apart. Plasma was generated at a steady monomer pressure of 0.3 torr at a current density of 1 mA/cm<sup>2</sup>. The discharge duration varied from 30 to 40 s. To maintain the same procedural conditions in all experiments, vapors of monomers of low sublimation pressure, such as octamethylcyclotetrasilazane and dedecamethylcyclohexasilane, were admixed with argon. The thickness of polymer films deposited under these conditions ranged from 0.1 to 1 μm.

### Infrared Spectroscopy

Infrared spectra of the polymer films were recorded on a Perkin-Elmer Model 457 Spectrophotometer, using the attenuated total reflection (ATR) technique.

### Gravimetric Measurements

Measurements of the changes in polymer weight during the aging process were performed for film samples with an initial weight of about 0.02 g deposited onto aluminum foil. The changes were monitored gravimetrically by using a Sartorius Electronic Digital Microbalance, Model 2600.

### Wettability Measurements

Wettability of plasma polymer films was determined by measuring the advancing contact angle of sessile drops of two test liquids: water and methylene iodide. The measurements were carried out at room temperature using a PZO goniometer eyepiece. Each type of plasma polymer was characterized by contact angle measurements performed for at least three polymer samples deposited in separate experiments. Reproducibility of the measurements was better than  $\pm 2^\circ$  in most cases.

To calculate the dispersion ( $\gamma_s^d$ ) and polar ( $\gamma_s^p$ ) components of the surface free energy ( $\gamma_s$ ) of plasma polymer films, the contact angle data were analyzed according to a model for low energy surfaces developed by Owens et al. [13].

### Materials

Prior to polymerization the monomers were purified by vacuum rectification or vacuum sublimation. Water and methylene iodide were triply distilled before the contact angle measurements.

## RESULTS AND DISCUSSION

### Changes in Film Structure

The effect of aging on the structure of plasma polymer films was documented by IR analysis. Since a detailed description of the spectra of plasma polymers under investigation has been published elsewhere [4, 14], the discussion here will be confined to those absorption bands important for the scope of this work.

Figure 1 represents the IR spectra of plasma-polymerized hexamethyldisilane (PP-HMDS) film shortly after deposition (Spectrum A) and following 2 months exposure to air (Spectrum B). By comparing the spectra, one may note qualitative and quantitative changes in several absorption ranges. The spectrum of the aged polymer film (Fig. 1B)

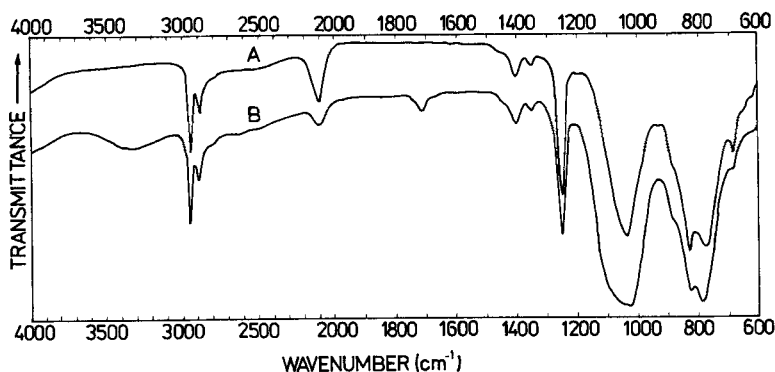


FIG. 1. ATR-IR spectra of plasma-polymerized hexamethyldisilane film; (A) before aging and (B) after exposure to the atmosphere for 2 months.

exhibits new absorption bands in the  $3600\text{--}3100\text{ cm}^{-1}$  and  $1720\text{ cm}^{-1}$  regions which are absent in the spectrum of the nonaged film (Fig. 1A). The band observed within the  $3600\text{--}3100\text{ cm}^{-1}$  range is typical of the stretching vibrations of the hydroxyl groups. However, the marked broadening noted for this band (Fig. 1B) indicates that it may arise from hydrogen-bonded hydroxyls from the Si-OH and C-OH groups or water [15]. The sharp band at  $1720\text{ cm}^{-1}$  (Fig. 1B) is attributed to the stretching vibration of the carbonyl group. Moreover, a decrease in the intensity of absorption at  $2100\text{ cm}^{-1}$  (Si-H, stretch) and significant broadening of the band at  $1100\text{--}1000\text{ cm}^{-1}$  are noted. The former spectral change evidently indicates a decrease in the content of SiH groups. The latter change is more complex and results from the formation of Si-O-Si and Si-O-C bonds during aging. The signals from the stretching vibrations of these bonds overlap with the absorption bands from  $\text{-CH}_2\text{-}$  wagging vibrations in the Si- $\text{CH}_2\text{-Si}$  and Si- $\text{CH}_2\text{-CH}_2\text{-Si}$  polymer crosslinks (Fig. 1A), which also fall in this region [4].

Figure 2 exemplifies the changes in the spectra of plasma-polymerized hexamethylcyclotrisilazane (PP-HMCTSN) film subjected to the atmospheric aging process. As previously, in the spectrum of the aged polymer (Fig. 2B) one can observe the appearance of the carbonyl bond at  $1720\text{ cm}^{-1}$  and an increase in its intensity with aging time (Figs. 2C and 2D). There are also marked changes in the absorption bands at  $2130\text{ cm}^{-1}$  (Si-H stretch),  $1175\text{ cm}^{-1}$  (N-H bend in Si-NH-Si groups), and in the  $1100\text{--}1000\text{ cm}^{-1}$  range ( $\text{-CH}_2\text{-}$  wag in Si- $\text{CH}_2\text{-Si}$  and Si- $\text{CH}_2\text{-CH}_2\text{-Si}$  links). In order to characterize the observed spectral changes quantitatively, absorption data were evaluated as the ratio of

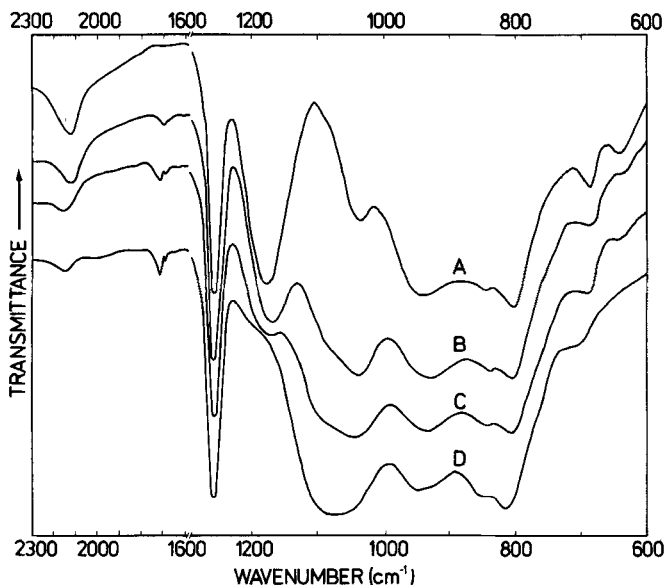


FIG. 2. ATR-IR spectra of plasma-polymerized hexamethylcyclotrisilazane film after various time of aging in the atmosphere: (A) before aging, (B) after 8 days, (C) after 14 days, and (D) after 30 days.

areas under the peaks,  $A/A_0$ , where  $A_0$  is the initial peak area and  $A$  is the area after a given time of aging. The relative intensity of IR absorption  $A/A_0$  for SiH ( $2130\text{ cm}^{-1}$ ), NH ( $1175\text{ cm}^{-1}$ ), and  $1100\text{--}1000\text{ cm}^{-1}$  bands is shown as a function of aging time in Fig. 3. The curves in this figure indicate very clearly that the concentration of SiH and NH groups in the polymer drops drastically with increasing aging time. The rise noted for the intensity of band at  $1100\text{--}1000\text{ cm}^{-1}$  is associated with an increasing concentration of Si-O-Si and presumably Si-O-C bonds which are produced during aging.

Based on the IR data, the formation of hydroxyl, carbonyl, and siloxane structural units and the decay of hydrosilyl groups appears to be a general trend in the structural changes involved in aging process for all the organosilicon plasma polymers investigated. The IR study is consistent with the results of elemental analysis [16, 17] and electron spectroscopy [18] which revealed relatively high concentrations of oxygen even in those plasma polymers produced from organosilicon monomers containing no oxygen atoms. It should also be noted that the formation of hydroxyl and carbonyl groups has been observed for the aging of plasma polymer films obtained from numerous hydrocarbons [11, 19].

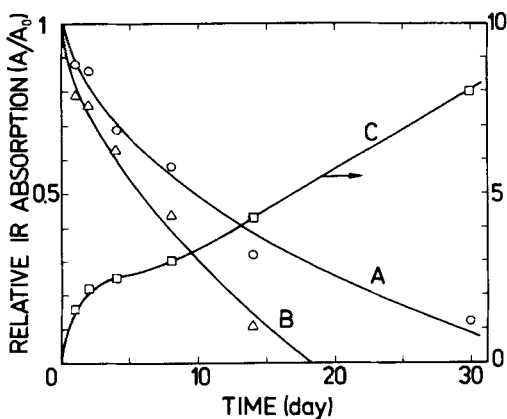
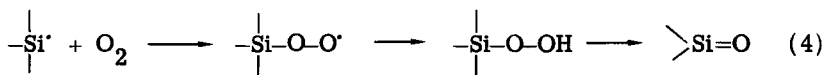
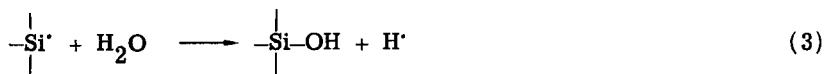
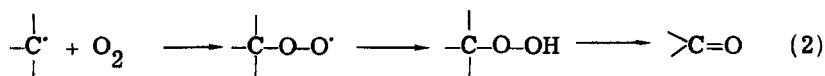
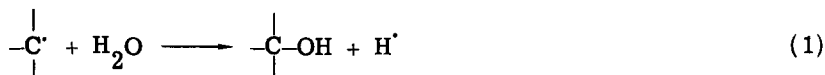


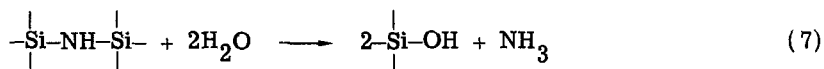
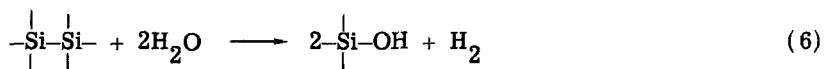
FIG. 3. Relative intensity of IR absorption  $A/A_0$  for: (A) SiH, (B) NH, and (C)  $1100\text{-}1000\text{ cm}^{-1}$  bands as a function of aging time.

### Mechanism of Aging

To explain the changes observed in the structure of aged plasma-polymerized organosilicon films, the elementary reactions which contribute to the aging process have to be considered. Since plasma polymer films are known to be very rich in free radicals [11, 20] and the lifetimes of these radicals are relatively long even under ambient conditions [20], they are believed to react with air-forming oxygen-containing groups in the surface layer. Alkyl and silyl radicals trapped in the structure of the plasma polymers investigated [4, 14] can undergo a variety of oxidation reactions with atmospheric water and oxygen, resulting in the formation of the observed hydroxyl and carbonyl groups as well as hydroperoxide groups:

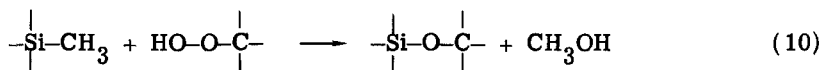
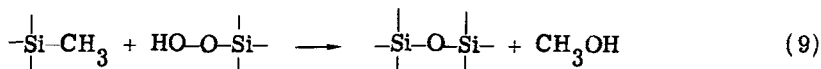
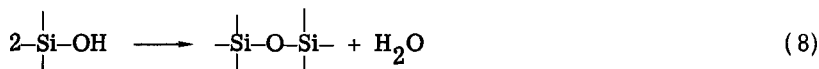


Furthermore, some reactive structural units present in organosilicon plasma polymers in contact with oxygen and water may be converted into silanol groups by oxidation and hydrolysis reactions [21]:



Reaction (5) leads to a decrease in the concentration of SiH groups of the plasma polymers investigated. Reaction (6) seems to be particularly important in the aging of silane plasma polymers which presumably contain a relatively large number of Si-Si bonds incorporated from the monomer structure. However, these bonds are also believed to be present in the structure of the remaining groups of plasma polymer films. Reaction (7) is responsible for the decay of the NH units observed in the case of the aging of silazane plasma polymers (Figs. 2 and 3).

Sinanol and hydroperoxide groups produced during aging may subsequently undergo various secondary condensation reactions leading to formation of Si-O-Si and Si-O-C bonds in the polymer film:



Reactions (8)-(10) account for the intensification and broadening of the absorption band in the 1100-1000  $\text{cm}^{-1}$  range as noted with aging time (Figs. 1 and 2).

In general, the reactions present satisfactorily describe the structural changes found in aged plasma polymer films and indicate the complex mechanism of the aging process.

### Kinetics of Aging

Kinetics of the aging process was characterized gravimetrically by measurements of the gain in weight of films resulting from the incorporation of atmospheric oxygen and water. The gravimetric data were expressed as the ratio  $\Delta W/W_0$ , where  $W_0$  is the initial weight of the film and  $\Delta W$  is the difference between the film weight after a particular aging time and the  $W_0$  value. Typical plots of the relative



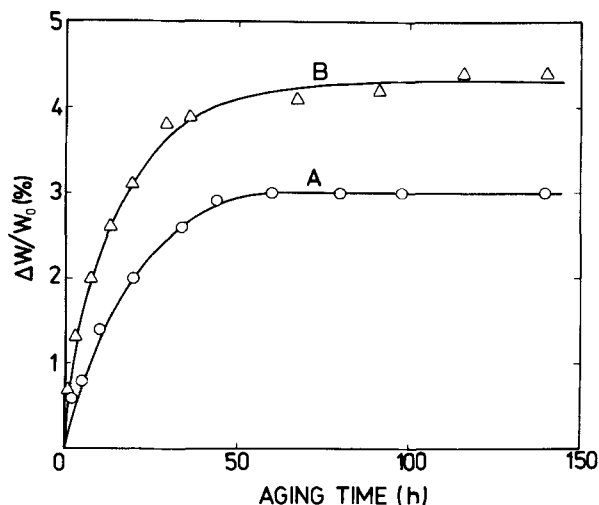


FIG. 4. Relative weight gain  $\Delta W/W_0$  as a function of aging time for plasma-polymerized hexamethylcyclotrisilazane films deposited at different current densities: (A) 1 and (B) 2.4 mA/cm<sup>2</sup>.

weight gain  $\Delta W/W_0$  vs aging time for PP-HMCTSN films produced at two different current densities are illustrated in Fig. 4. The curves in the figure show that the weight gain of film rises rapidly in the initial stage of aging, reaching a "plateau" value after roughly 50 h. This is in agreement with the kinetics of radicals decay in organo-silicon plasma polymer films exposed to the atmosphere, which revealed that the decay process was fastest in the initial stages [20]. Furthermore, by comparing the  $\Delta W/W_0$  values for the "plateau" region in both curves, it is noted that the weight gain increases with the current density. This trend corresponds to the rise in radical concentration [22] and the resulting increase of oxygen content [16] in organo-silicon plasma polymer films due to increasing discharge power or current density.

The shape of the kinetic curves in Fig. 4 suggests that the aging process is controlled by the diffusion of molecular oxygen and water into the film. The linear plots of  $\Delta W/W_0$  vs the square root of the aging time ( $t$ ) found for the initial nonsteady conditions (see Fig. 5) in terms of diffusion theory [23] fully confirm this assumption. The increase in the slope of plots of  $\Delta W/W_0$  vs  $\sqrt{t}$  with current density, noted in Fig. 5, seems to be reasonable since, as was mentioned earlier, the increase in this parameter enhances radical concentration in the film, thus increasing the rate of the aging process.

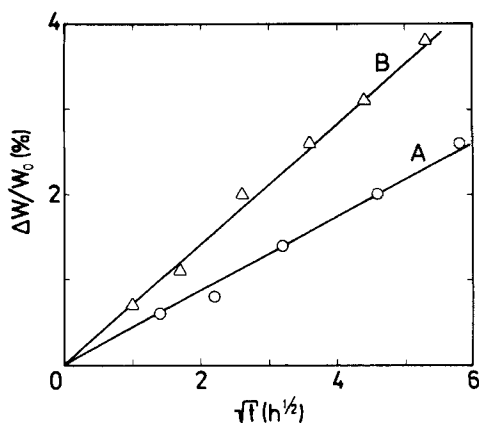


FIG. 5. Plots of relative weight gain  $\Delta W/W_0$  vs square root of aging time.

#### Effect of Aging on Surface Free Energy

To evaluate the effect of aging on wettability properties, the contact angles were measured on films after their exposure to the atmosphere for various time periods. The most significant changes in wettability were observed during the first two days of aging, and after this period the effect of aging decreased considerably. This was consistent with the kinetics of aging (Fig. 4) which indicated that the most rapid weight gain of film took place within the initial stage up to 50 h.

The surface free energy values evaluated for freshly deposited films and after their aging for 48 h are summarized in Table 1, Columns A and B, respectively. The changes in the surface energy properties resulting from the aging effect are illustrated in Column C of Table 1. From these data it is evident that aging of the polymer films investigated involves an increase in the polar component ( $\gamma_s^p$ ) whereas the dispersion component ( $\gamma_s^d$ ) appears to decrease. This trend seems to be characteristic of plasma-polymerized materials since similar changes in the surface energy components have been observed for the aging of numerous hydrocarbon plasma polymer films [24].

The rise in  $\gamma_s^p$  is attributed to the formation of strong hydroxyl and carbonyl polar groups in the surface structure of the films, as was proved by IR spectroscopy and described by Reactions (1)-(7). The decrease in  $\gamma_s^d$  may derive from the reduced crosslink density

TABLE 1. Effect of Aging on the Surface Free Energy of Plasma Polymer Films Deposited from Various Organosilicon Monomers

Monomer	Structural formula	Surface energy, erg/cm <sup>2</sup>											
		A. Before aging				B. After aging				C. Change†			
		$\gamma_s$	$\gamma_s^*$	$\gamma_s^p$	$\gamma_s^d$	$\gamma_s$	$\gamma_s^*$	$\gamma_s^p$	$\gamma_s^d$	$\Delta\gamma_s$	$\Delta\gamma_s^p$	$\Delta\gamma_s^d$	
Hexamethyldisilane	(Me <sub>3</sub> Si) <sub>2</sub>	30.7	32.6	1.9	30.1	5.3	35.4	-0.6	+3.4	+2.8			
Dodecamethylcyclohexasilane	(Me <sub>2</sub> Si) <sub>6</sub>	34.3	41.4	7.1	28.1	13.1	41.2	-6.2	+6.0	-0.2			
Hexamethyldisilazane	(Me <sub>3</sub> Si) <sub>2</sub> NH	28.3	32.9	4.6	24.2	12.6	36.8	-4.1	+8.0	+3.9			
Hexamethylcyclo-tri-silazane	(Me <sub>2</sub> SiNH) <sub>3</sub>	30.1	35.4	5.3	22.6	9.3	31.9	-7.5	+4.0	-3.5			
Octamethylcyclo-tetra-silazane	(Me <sub>2</sub> SiNH) <sub>4</sub>	38.0	45.0	7.0	33.4	10.4	43.8	-4.6	+3.4	-1.2			
Hexamethyldisiloxane	(Me <sub>3</sub> Si) <sub>2</sub> O	27.4	29.1	1.7	25.4	3.9	29.3	-2.0	+2.2	+0.2			
Hexamethylcyclo-tri-siloxane	(Me <sub>2</sub> SiO) <sub>3</sub>	25.7	27.5	1.8	25.0	2.7	27.7	-0.7	+0.9	+0.1			
Octamethylcyclo-tetra-siloxane	(Me <sub>2</sub> SiO) <sub>4</sub>	25.7	27.5	1.8	25.2	2.4	27.6	-0.5	+0.6	+0.1			

\*  $\gamma_s = \gamma_s^d + \gamma_s^p$ .

† Changes are based on values for aged polymer films.

in the surface region [24] due to the hydrolysis reactions (Eqs. 6 and 7). The much smaller changes in both surface energy components of siloxane plasma polymers as compared to those for silane and silazane polymers (Table 1, Column C) presumably result from the high stability of the siloxane bond in the aging process and the relatively low concentration of radicals in this group of polymers. The results of ESR analysis by Yasuda and Hsu [20] have shown that the radical concentration in plasma-polymerized hexamethyldisiloxane only half that in the plasma polymer of hexamethyldisilane.

## CONCLUSIONS

The results presented in this paper indicate the important aspects of the aging process in organosilicon plasma polymer films are as follows:

1. The formation of  $-\text{OH}$ ,  $>\text{C}=\text{O}$ ,  $\text{Si}-\text{O}-\text{Si}$ ,  $\text{Si}-\text{O}-\text{C}$  groups and the decay of  $\text{SiH}$  groups appear to be general trends in the structural changes of the plasma polymer films investigated.
2. The aging process proceeds via a complex mechanism comprising various reactions of atmospheric oxygen and water with alkyl and silyl radicals as well as with some reactive bonds present in the film structure.
3. Kinetic studies have proved that the aging process is controlled by the diffusion of oxygen and water molecules from the atmosphere into the film.
4. Aging produces distinct changes in the components of the surface free energy of the film by increasing the polar component and decreasing the dispersion component. This trend has been found to be correlated with structural changes in the film resulting from aging.

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