

Atmospheric Plasma Deposited Films from Several Organosilanes and Differences in Chemical Structure and Si-O-Si Bonding Arrangements

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Abstract: Atmospheric Plasma Enhanced Chemical Vapor Deposition (APECVD) is used to prepare films from hexamethyldisiloxane (HMDSO), tetraethoxysilane (TEOS), methyltriethoxysilane (MTES), decamethylcyclopentasiloxane (D5), bis(trimethoxysilyl) hexane (BTMSH), and phenyltriethoxysilane (PHTES). Fourier Transform IR (FTIR) spectroscopy shows chemical features of the precursors in the films and deconvolution of the Si-O-Si band reveals different bonding structures, as well as changes with conditions.

Keywords: PECVD, atmospheric plasma, organosilicon precursors, IR spectroscopy.

1. Introduction

Organosilane materials are used industrially for a wide variety of coatings, surface modification, and films in industries spanning automotive, electronics, aerospace, consumer goods, medicine and life sciences, and more. Many processes, including sol-gel, UV-cured coatings, and silane coupling, involve preparation from liquid compounds to create a relatively thick coating. Plasma Enhanced Chemical Vapor Deposition (PECVD) of organosilicon precursors, however, is used to create thin films for dielectric layers, adhesion promotion, barrier and selective permeation, corrosion protection, tailoring surface energy, and abrasion resistance [1-11].

PECVD of organosilanes can produce bonding structures of the Si-O-Si that include cross-linked networks of linear chains with and without terminal and side groups, stoichiometric SiO₂ in a relaxed network structure, ring structures, as well as larger cage-type structures with a range of porosity. Organic side-groups that are terminal groups of or cross-linked in the network can also be present. With numerous organosilane compounds available, countless varieties of chemical features and bonding arrangements are possible. These features and structures determine the film properties that ultimately determine functionality, such as hardness and abrasion resistance, barrier properties, selective permeation, electrical properties, optical properties, hydrophilicity and hydrophobicity, and more.

This study evaluates PECVD films and bonding structures obtained from different organosilicon precursors that are not common for PECVD. Effects of cyclic vs. linear siloxanes, siloxanes vs. alkoxysilanes, substitution of alkoxy groups for organic groups, as well as mono- vs. di-podal structures are analyzed. FTIR is used to compare chemical features and Si-O-Si bonding arrangements of the films. Understanding these types of effects can help to provide direction for tailoring properties of the films for different applications.

2. Experimental

Substrates were Si wafers (p-type) cut into a size of approximately 15 x 15 mm. HMDSO, TEOS, MTES, BTMSH, and PHTES were donated by Shin-Etsu

Chemical Co., Ltd, while D5 was supplied by Gelest. In-house compressed air was used as the ionizing gas, which was filtered and regulated at a pressure of 5 bar before entering the plasma generation unit. Nitrogen (> 99%) from Praxair was used as a carrier for the precursor.

The atmospheric pressure plasma system was supplied by Plasmatec® and consists of a pulsed plasma source. Air was delivered at a rate of 2,400 standard L/h. The reference voltage was set at 70–100%, while the output voltage ranged from 235–350 V and the duty ranged from 70–100%. The precursor was injected into a port attached downstream from the exit of the plasma jet. The precursor was delivered using a NE-300 syringe pump from New Era Pump Systems at a rate between 5–40 g/h. Nitrogen at 2 L/min was used as a carrier gas for the precursor and was fed into the precursor delivery system downstream from a cartridge heater for evaporation. The jet scanned over the stationary substrates in the x- and y-directions using a motor, in which the scan speed was set at 1 m/min and distance between scan paths was 4 mm. The distance between the plasma exit port and the substrate surface was held constant at 15 mm and each sample was scanned twice.

Chemical bonding information was obtained using an Attenuated Total Reflectance (ATR) Fourier Transform Infrared Spectrometer (FTIR). A Nicolet 6780 FTIR by Thermo Scientific was used for this study with a range of 400–4,000 cm⁻¹.

3. Results and Discussion

Films were prepared with each precursor and the thickness ranged from 1.2 - 2.4 μm. Samples were analyzed with FTIR and the peak associations used to identify the functional groups and bonding structures in the films are provided in Table 1.

Fig. 1 shows the FTIR transmittance spectra for the precursors using the lowest energy input (922 W) and highest flow rate, 40 g/h. This condition represents a relatively low value of the normalized energy input parameter for this system, W/FM , defined by Yasuda [23,24], in which FM represents the mass flow rate of the precursor. In this region, the system has excess reagent and limited energy, in which fragmentation is lower and it

is more likely the films retain some features of the precursor molecule.

Table 1. Peak Assignments for the FTIR Spectra [12-22]

Group*	Frequency (cm ⁻¹)
<u>$\nu(\text{C-H})$</u>	3000-2800
<u>Si-CH_3</u>	
$\delta_a(\text{CH}_3)$	1440-1390
$\delta_s(\text{CH}_3)$ in T unit $[\text{Si}(\text{CH}_3)\text{O}_3]$	1275-1270
$\delta_s(\text{CH}_3)$ in D unit $[\text{Si}(\text{CH}_3)_2\text{O}_2]$	1265-1260
$\rho(\text{CH}_3)$ and $\nu(\text{Si-C})$	865-750
<u>$\text{Si-(CH}_2)_x(\text{CH}_3)$</u>	
$\delta(\text{CH}_3)$ in C- CH_3	1460 and 1375
$\delta(\text{Si-CH}_2-)$ scissors	1420-1400
$\delta(-\text{CH}_2-)$ in SiCH_2CH_3	1250-1220
$\delta(-\text{CH}_2-)$ in $\text{Si}(\text{CH}_2)_2\text{CH}_3$	1220-1200
$\delta(-\text{CH}_2-)$ in $\text{Si}(\text{CH}_2)_3\text{CH}_3$	1200-1190
$\delta(-\text{CH}_2-)$ in $\text{Si}(\text{CH}_2)_{x>3}\text{CH}_3$	1190-1170
$\nu(\text{Si-C})$	830-750
<u>Si-phenyl</u>	
aromatic overtones	2000-1650
$\nu(\text{C=C})$ in ring	1600-1590
$\delta(\text{Si-Ph})$	1430
Si-Ph	1130-1110
$\delta(\text{C=C})$	~1000
$\delta(\text{Ph})$ two or more bands	760-690
<u>$\nu(\text{Si-O-Si})$</u>	<u>1250-980</u>
Highly porous cage structure or Si-O-C groups	1250-1180
Rings or cage structures with higher bond angles up to $\sim 150^\circ$	1180-1112
Network of short structures or stoichiometric SiO_2 with bond angle $\sim 144^\circ$ (1080 cm^{-1})	1110-1080
Linear chains or branched network with side groups, Si-O-Si angles $< 144^\circ$	1075-1023
$\nu(\text{Si-O-C})$	1190-1106
<u>-OH groups</u>	
$\nu(\text{-OH})$ Si-OH terminal group	3700-3600
$\nu(\text{-OH})$ Si-OH in a chain, H-bonded	3650-3200
$\nu(\text{Si-O})$ in Si-OH	950-830
$\nu(\text{-OH})$ adsorbed water	3500-3300
$\delta(\text{-OH})$ adsorbed water	1630

*Vibrational modes: ν =stretching, δ =bending, ρ =rocking, a =asymmetric, and s =symmetric

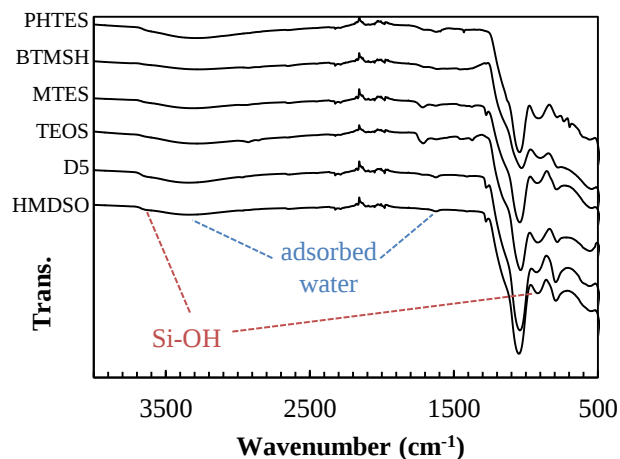


Fig. 1. FTIR spectra from 4000-500 cm⁻¹ for films prepared at 83 kJ/g.

For all of the films in the region 3800-3200 cm⁻¹, a broad band appears around 3300 cm⁻¹, as well as a peak around 1625 cm⁻¹, which are associated with adsorbed water. Peaks associated with Si-OH are also present for all of the films around 3640 cm⁻¹ and 920 cm⁻¹. Fig. 2 shows the range of 1800-500 cm⁻¹ to observe the peaks in this region. In the Si-O-Si region, all films show the main peak in the range of 1046-1030 cm⁻¹, with shoulders at higher frequencies. This main peak is indicative of network structures of branched chains with some Si atoms containing side groups, producing bond angles $< 144^\circ$.

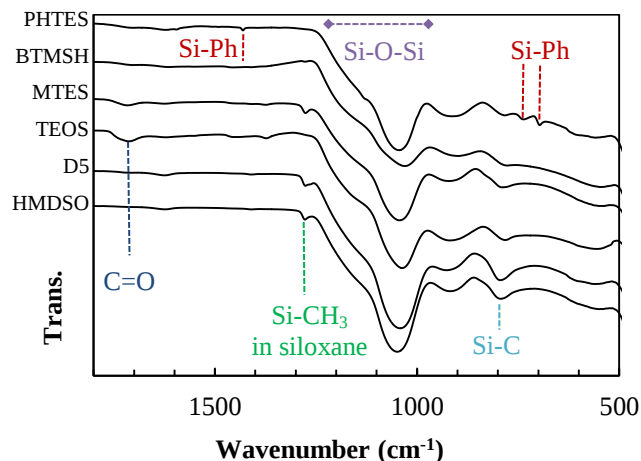


Fig. 2. FTIR spectra from 1800-500 cm⁻¹ for films prepared at 83 kJ/g.

Comparing HMDSO and D5, both are very similar and show peaks for Si-CH₃ around 1410 cm⁻¹, 1277 cm⁻¹ and 793 cm⁻¹. Although D5 is cyclic and HMDSO is linear, it appears for the deposition system in the range of conditions tested, both are in the same class and HMDSO can be replaced with the safer chemical, D5, with respect to flammability and environmental impact.

Two ethoxy silanes, TEOS and MTES, show an additional peak around 1715 cm⁻¹, which is associated with carbonyl groups. Furthermore, two peaks at 1455

cm^{-1} and 1375 cm^{-1} are present in the TEOS and MTES, which is generally associated with C-CH_3 groups. Note that $\text{Si-OCH}_2\text{CH}_3$ groups are not present in the films, as the spectra do show a peak at $970\text{-}940\text{ cm}^{-1}$, which is associated with this group. The main difference between TEOS and MTES is the peak associated with Si-CH_3 at 1277 cm^{-1} , which is visible for MTES, but shows a very small bump for TEOS. The Si-O-Si regions for HMDSO, D5, TEOS, and MTES are somewhat similar, indicating similar structures and bonding arrangements.

The BTMSH film shows a very small bump at 1277 cm^{-1} , indicative of Si-CH_3 groups. Furthermore, peaks indicative of Si-alkyl groups are present at 1455 cm^{-1} and 1375 cm^{-1} , as well as 1410 cm^{-1} and 777 cm^{-1} . The peak $1250\text{-}1170\text{ cm}^{-1}$ is useful in determining the length of the alkyl group. However, the Si-O-Si band overlaps heavily in this region. Deconvolution of the peaks in this region was performed in order to reveal the peak location and is presented later.

It is clear from the PHTES peak that phenyl groups are present in the film. Weak bands associated with aromatic overtones were observed at 1701 cm^{-1} and 1689 cm^{-1} when zooming into the region. Other peaks indicative of the Si-phenyl group were also observed, including 1595 cm^{-1} , 1430 cm^{-1} , 737 cm^{-1} , and 697 cm^{-1} . Shoulders on the Si-O-Si peak around 1130 and 1000 cm^{-1} were also observed.

In order to evaluate the changes in Si-O-Si bonding structures, the absorbance bands in the region around $1300\text{-}1000\text{ cm}^{-1}$ were deconvoluted into overlapping Gaussian curves to represent the different bonding structures. Figs. 3-8 show the deconvoluted absorbance spectra for the films prepared using 83 kJ/g .

All of the films show four peaks that are associated with different Si-O-Si bonding structures. The main peak for all of them is around 1038 cm^{-1} and represents a network of cross-linked chains and side groups, with a Si-O-Si bond angle $< 144^\circ$. Another peak associated with network structures is present at 1082 cm^{-1} which is associated with stoichiometric SiO_2 with bond angles around 144° . A strong peak around 1145 cm^{-1} present on all samples is indicative of cage structures, as well as a peak around 1204 cm^{-1} associated with highly porous cages. While quantification of the deconvoluted peaks should be taken with caution, the area ratios of the sum of the two lower frequency Si-O-Si peaks to the two higher frequency peaks representing cage structures are similar for HMDSO, D5, TEOS, and MTES around 3. BTMSH, however, has a ratio higher than 4 due to the increased contribution from the network peak. It is possible that the di-podal feature of the molecule contributes to this. PHTES, however, had the lowest ratio, due to the increase in the cage structures.

All of the spectra show a peak of some size at 1277 cm^{-1} , indicative of Si-CH_3 groups in T units. In addition, HMDSO and D5 showed a peak at 1265 cm^{-1} associated with D units. Although the Si-CH_3 peak was very low for

TEOS, BTMSH, and PHTES, its presence indicates that T units are formed in the plasma process.

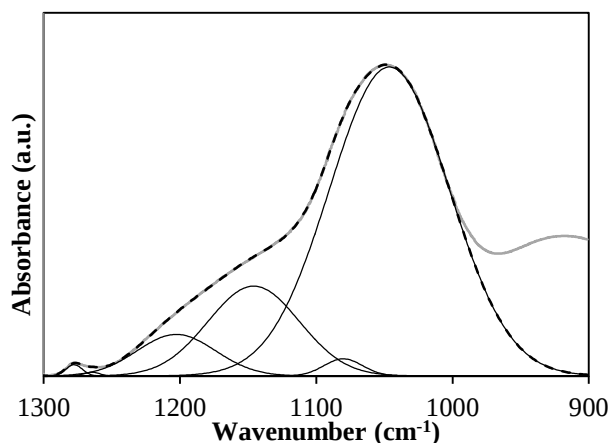


Fig 3. Peak fits of the $1300\text{-}1000\text{ cm}^{-1}$ band for HMDSO.

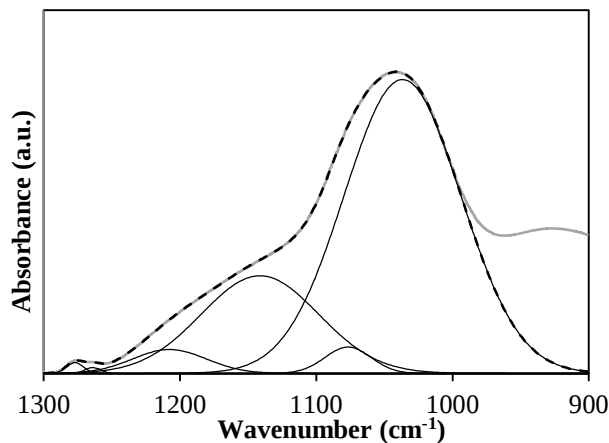


Fig 4. Peak fits of the $1300\text{-}1000\text{ cm}^{-1}$ band for D5.

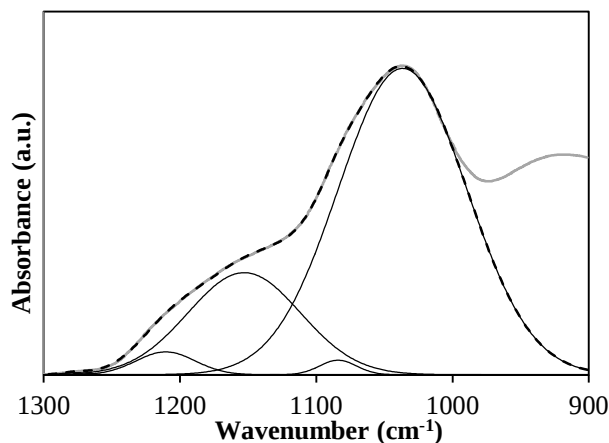


Fig. 5. Peak fits of the $1300\text{-}1000\text{ cm}^{-1}$ band for TEOS.

The deconvolution of the BTMSH peak confirms the presence of Si-alkyl groups with the 1225 cm^{-1} peak. This frequency is associated with $\text{Si-CH}_2\text{CH}_3$, which points to cleavage of the alkyl bridge to form mostly ethyl, as well as some methyl groups. For PHTES, The other peaks associated with Si-Ph appear in the deconvoluted peaks at 1131 and 993 cm^{-1} .

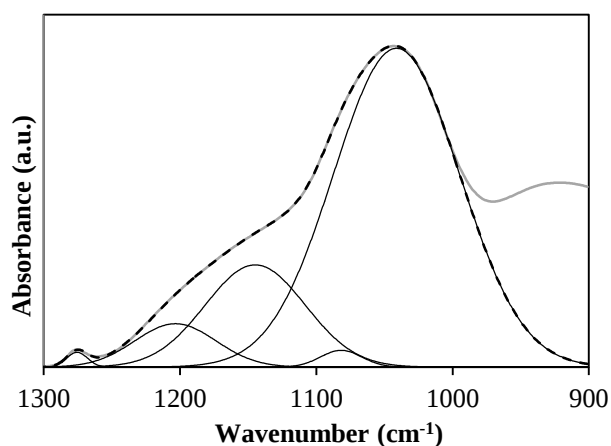


Fig. 6. Peak fits of the 1300-1000 cm^{-1} band for MTES.

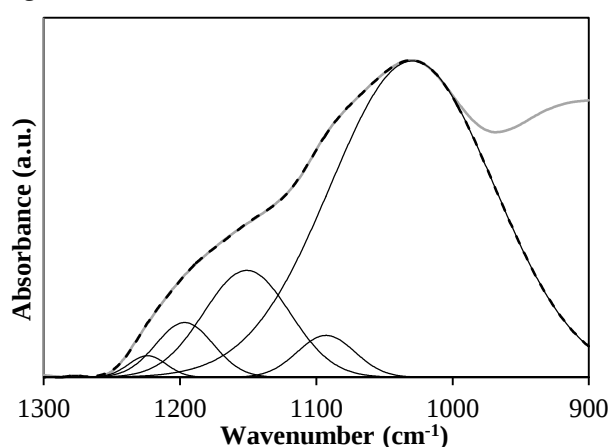


Fig. 7. Peak fits of the 1300-1000 cm^{-1} band for BTMSH.

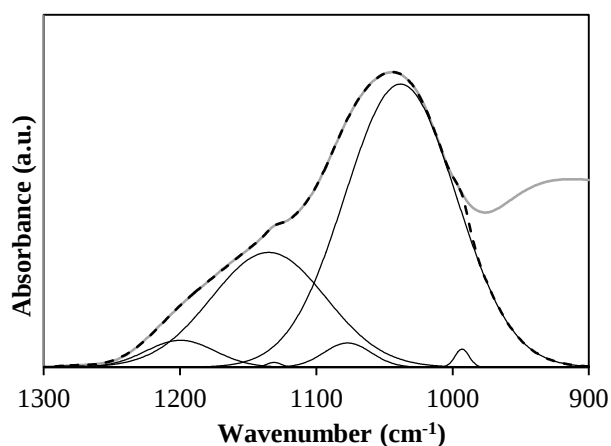


Fig. 7. Peak fits of the 1300-1000 cm^{-1} band for PHTES.

4. Conclusions

Films were prepared from atmospheric pressure plasma PECVD using several organosilane precursors. FTIR revealed multiple Si-O-Si bonding arrangements for all films. Chemical groups in the precursors are present in the films, especially at lower W/FM. The comparisons show how chemical features of the organosilane precursor compound can bring about unique film chemistry and structures, enabling tailoring of the films for the desired properties and functionalities.

5. References

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