

Mechanisms of plasma polymerization of various silico-organic monomers

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Abstract

The plasma polymerization of hexamethyl disiloxane (HMDSO), divinyltetramethyl disiloxane (DVTMDSO), and octamethyl cyclotetrasiloxane (OMCATS) was investigated using either argon or argon/oxygen mixtures as reactants. With argon, different mechanisms of polymerization for each polymer were identified reflecting its respective nature. For HMDSO, formation of Si-CH₂-Si bonds plays a decisive role, whereas in DVTMDSO Si-(CH₂)₄-Si bridges are formed. In both cases a second mechanism exists leading to the loss of SiC_xH_y groups. Finally, OMCATS polymerizes via the formation of polymethylsiloxane chains and rings. These various mechanisms result in differences in the properties of the polymer films. In contrast, almost inorganic films were obtained with oxygen irrespective of the monomer. An investigation of the deposition kinetics shows that the plasma power and the monomer evaporation temperature are the decisive parameters determining the polymer growth rates. A comparison of direct and remote plasma reaction reveals that in the cases of HMDSO and OMCATS direct plasma dissociation is necessary to promote the polymerization process, whereas DVTMDSO also polymerizes under remote conditions.

1. Introduction

During the last years, silico-organic plasma-polymerized thin films have attracted increasing interest for applications in such diverse fields as optics, electronics, sensors, and biomedicine [1]. This is mainly owing to the fact that important properties of these films can be varied widely by a suitable choice of source monomer and deposition parameters. Moreover, many silico-organic monomers are sufficiently volatile, non-toxic and non-flammable, and relatively cheap [1].

In many cases silico-organic polymer films have to meet a long list of requirements with respect to their properties. In order to design a film and its deposition process in view of a special application, an increased understanding of the correlations between the monomer and the polymerization conditions used, the respective mechanisms of polymerization, and the resulting film composition and properties is required. There are numerous papers on plasma-polymerized silico-organic films published in the literature (for a review see ref. 1). However, a great many of them deal with the well

investigated hexamethyl disiloxane and hexamethyl disilazane; therefore, the influence of the nature of the monomer [2–5] still deserves closer investigation.

As a contribution to this question we studied the plasma polymerization of hexamethyl disiloxane (HMDSO), divinyltetramethyl disiloxane (DVTMDSO), and octamethyl cyclotetrasiloxane (OMCATS) (see Table 1) using the remote plasma-enhanced chemical vapour deposition (PECVD) technique. In this technique [6–8] the monomers are not plasma dissociated but react with excited species extracted from a spatially remote plasma. Thus, random dissociation of monomer molecules is avoided. This leads in many cases to a reduction of reaction pathways and to improved process control [6, 8]. In contrast, by increasing the r.f. power to a point where the plasma reaches into the reaction zone, direct plasma excitation of the monomers can be accomplished. Thus remote and direct plasma polymerization can therefore be studied using the same set-up.

The choice of the three monomers studied was motivated as follows. Since the plasma polymerization of HMDSO is well documented in the literature (see ref. 1 and refs. cited therein, and refs. 9 and 10), it may serve as a standard in order to compare our results with those from other techniques. With respect to HMDSO,

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TABLE 1. Silico-organic monomers used in our study

Monomer	Formula	Acronym
Hexamethyldisiloxane	$(\text{Me}_3\text{Si})_2\text{O}$	HMDSO
1,3-Divinyl 1,1,3,3-tetramethyldisiloxane	$((\text{H}_2\text{C}=\text{CH})\text{Me}_2\text{Si})_2\text{O}$	DVTMDSO
Octamethylcyclotetrasiloxane	$(\text{Me}_2\text{SiO})_4$	OMCATS

Me = CH_3 .

OMCATS already consists of a silicon/oxygen skeleton. Therefore, the character of the polymer films is expected to be more inorganic under similar conditions which should result for example in increased hardness. On the contrary, the DVTMDSO may polymerize via its vinyl groups. Highly crosslinked films may therefore be expected with a high organic character and properties such as chemical inertness.

Argon, oxygen, and mixtures of these two gases were used as reactants. Whereas excited Ar species are expected to react with the monomers physically by simply transferring energy, O_2 and excited oxygen species obviously will react chemically thereby increasing the inorganic character of the polymers.

This paper is the first part of two reports. It focusses on film composition and mean properties of polymers from various monomer/reactant mixtures (Section 3) and on deposition kinetics (Section 4). Models for the polymerization mechanisms are also proposed.

A detailed discussion of relevant film properties (e.g. hardness, stress, adhesion, transparency, chemical stability) and their dependence on deposition parameters will be published in a separate paper [11].

2. Experimental details

2.1. Experimental set-up

The plasma polymerization was carried out in a commercial remote PECVD system (PLASMOX IIa, Plasmos, Munich) which has previously been described in detail [8, 12]. The main components are a quartz tube serving as a plasma chamber and a stainless steel reaction/deposition chamber with a gas dispersal ring

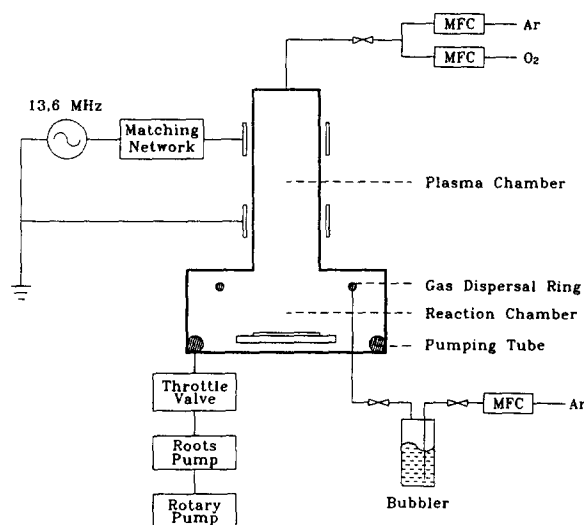


Fig. 1. Schematic drawing of the R-PECVD set-up used throughout this study.

and a pumping tube as shown in Fig. 1. The system is evacuated by means of a roots blower and a two-stage rotary pump. The plasma is capacitively coupled into the quartz tube with a 13.56 MHz generator. The monomers were temperature controlled in double-walled quartz bubblers which were connected to the gas dispersal ring. Argon was used as a carrier gas to transport the source gases into the reaction chamber. The flows of carrier gas and excitation gas were controlled by mass flow controllers (MFCs). Table 2 summarizes the deposition parameters used throughout these experiments.

With this design, two different modes of plasma excitation can be applied. In the low r.f. power range (< 30 W) the plasma is confined within the plasma

TABLE 2. Deposition parameters throughout our experiments

	HMDSO	DVTMDSO	OMCATS
Bubbler temperature ($^{\circ}\text{C}$)	-28.5	-15	16.5
Monomer partial pressure (mbar)	0.014	0.004	0.004
R.f. power (W)		14-200	
Substrate temperature ($^{\circ}\text{C}$)		90-100	
Pressure (mbar)		0.22-0.24	
Carrier gas flow (sccm)		65-100	
Source gas flow (sccm)		100-210	

chamber so only the excitation gas is plasma excited, and the monomer will react downstream with these excited species (remote plasma mode). In the high power region, the plasma extends well into the reaction chamber, and direct plasma dissociation of the monomer molecules will play an important role (direct plasma mode). By this means it is possible to evaluate the contributions of plasma dissociation of the monomer molecules and of their reactions with the excitation gas, respectively, to the polymerization process. (For details of the remote technique see refs. 6, 8 and 13.)

The monomers HMDSO (Merck-Schuchard), OM-CATS (Fluka Chemika) and DVTMDSO (PCR Research Chemicals Inc.) were used without further purification for the deposition on (100)Si substrates.

2.2. Film characterization

Ellipsometry (SD 2300, Plasmos) and interferometry (Leitz MPV-SP) were used for thickness measurements as well as for the determination of the refractive index of the films. Densities of some representative deposits were determined by weighing the samples, etching off the films and weighing again the bare substrates. Absorption spectra of the polymers were recorded with a FTIR spectrometer (BIORAD FTS 60A) in the transmission mode. For further characterization of the film composition, elemental analysis (EA) and Auger electron spectroscopy (AES) were employed.

3. Film Composition and Film Properties

3.1. Argon as excitation gas

We will first discuss the films obtained with argon as excitation gas. As will become evident, the mechanisms of polymerization are different for the three monomers investigated. Therefore, it is necessary to discuss them separately.

3.1.1. HMDSO

Figure 2 shows the FTIR transmission spectra of the HMDSO monomer and of a polymer film deposited with an r.f. power of 100 W and argon as excitation gas.

There are several characteristic differences between the two spectra which are due to the polymerization process. In the polymer, the carbon content (with respect to the Si-O-Si bonds) is lower. In contrast, the Si-O-Si asymmetric stretching peak (ASM) at 1050 cm^{-1} is broadened, and there are three peaks not found in the monomer spectrum: SiH (2140 cm^{-1}), $\text{Si}(\text{CH}_3)_2$ (800 cm^{-1}), and Si-CH₂-Si (1350 cm^{-1} , see also Fig. 3). Despite its weakness, the latter (owing to CH₂ scissor vibrations) is of special importance. It is usually accompanied by a much stronger band owing to the CH₂ wagging mode in the $1080\text{--}1040\text{ cm}^{-1}$ region

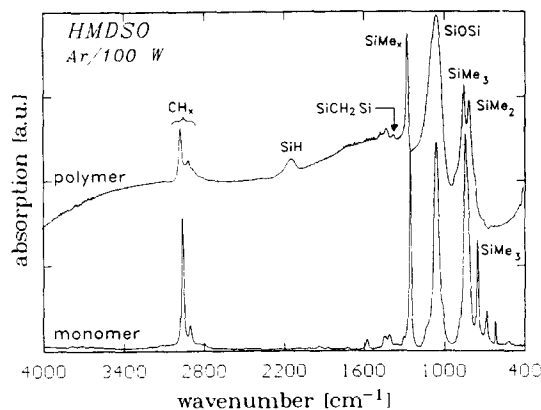


Fig. 2. FTIR transmission spectra of the HMDSO monomer and of a polymer film deposited at 100 W using Ar as the excitation gas. Only those peaks are labeled which are relevant to our discussion. A complete identification of the peaks is given in Table 3. The low wavenumber section of the polymer spectrum is shown enlarged in Fig. 3.

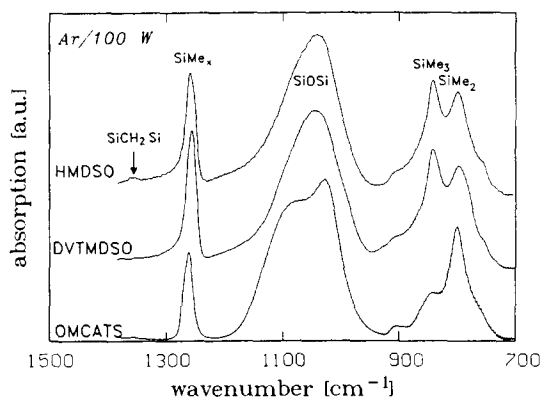


Fig. 3. Comparison of the spectra of the Ar/100 W polymer films from the three monomers in the wavenumber range $1500\text{--}700\text{ cm}^{-1}$.

[14]. However, in the case of oxygen-containing polymers such as the HMDSO films under discussion, this CH₂ wagging peak is masked by the Si-O-Si ASM peak. It is, however, found, for example, in the spectra of oxygen free hexamethyl disilazane plasma polymers [3]. From a comparison of the intensities of the 1350 cm^{-1} scissors peak and the 1060 cm^{-1} wagging peak in these silazane polymer spectra [15] it is evident that the very existence of the small 1350 cm^{-1} peak proves the building of Si-CH₂-Si bridges to be at least one of the polymerization mechanisms of the HMDSO/Ar process.

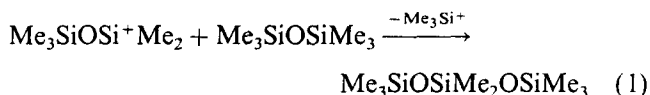
If this would be the only mechanism the ratio Si:O should be 2 (as in the monomer). However, this is not the case as is evident from the results of an elemental analysis of this film presented in Table 4. Thus there must be a second mechanism of crosslinking which is responsible for the excess loss of SiC_xH_y species.

TABLE 3. IR bands found in the spectra of the monomers and polymer films of our study

σ (cm ⁻¹)	Mode	Comment	Ref.	σ (cm ⁻¹)	Mode	Comment	Ref.
<i>CH_x correlated peaks</i>				<i>OH correlated peaks</i>			
2960	$\nu_{\text{CH}_3}^{\text{a}}$		[21, 22]	3650	ν_{OH}	free SiOH	[23]
2900	$\nu_{\text{CH}_3}^{\text{s}}$		[21, 22]	3400	ν_{OH}	H-bonded OH	[23]
2925	$\nu_{\text{CH}_2}^{\text{a}}$		[21, 22]	930	ν_{SiO}	in Si-OH	[14]
2855	$\nu_{\text{CH}_2}^{\text{s}}$		[21, 22]				
1460	$\delta_{\text{CH}_2}^{\text{a}}$		[21, 22]	<i>Si-O-Si correlated peaks</i>			
<i>Si-CH₂ correlated peaks</i>				1050	$\nu_{\text{SiOSi}}^{\text{a}}$	in Si-OH	[14]
1360	δ_{CH_2}	in Si-CH ₂ -Si	[14]	<i>Vinyl correlated peaks</i>			
1400	δ_{CH_2}	in Si-(CH ₂) ₂ -Si	[14]	3060	$\nu_{\text{CH}_2}^{\text{a}}$	in vinyl groups	[14]
<i>Si-CH₃ correlated peaks</i>				3020	$\nu_{\text{CH}_2}^{\text{s}}$	in vinyl groups	[14]
1410	$\delta_{\text{CH}_3}^{\text{a}}$	in Si-Me _x	[14]	1910	$\omega_{\text{CH}_2}^{\text{s}}$	in vinyl groups	[14]
1260	$\delta_{\text{CH}_3}^{\text{s}}$	in Si-Me _x	[14]	1600	$\nu_{\text{C}-\text{C}}$	in vinyl groups	[14]
845	$\rho_{\text{CH}_3}, \nu_{\text{SiC}}$	in Si-Me ₃	[14]	1400	δ_{CH_2}	in vinyl groups	[14]
760	$\rho_{\text{CH}_3}, \nu_{\text{SiC}}$	in Si-Me ₃	[14]	1010	$\tau_{\text{C}-\text{C}}$	in vinyl groups	[14]
885	$\rho_{\text{CH}_3}, \nu_{\text{SiC}}$	in Si-Me ₂	[14]	950	ω_{CH_2}	in vinyl groups	[14]
805	$\rho_{\text{CH}_3}, \nu_{\text{SiC}}$	in Si-Me ₂	[14]	700	ω_{CH_2}	in vinyl groups	[14]
775	$\rho_{\text{CH}_3}, \nu_{\text{SiC}}$	in Si-Me ₁	[14]	610	Si-CH=CH ₂	in vinyl groups	[14]
<i>Si-H correlated peaks</i>							
2140	ν_{SiH}		[14]				

ν , δ , ρ , ω , τ denote stretching, bending, rocking, wagging, and twisting modes, respectively, a and s asymmetric and symmetric vibrations.

In their work on the mechanisms of polymerization of HMDSO Wrobel and coworkers [1, 3] have proposed that after ionization of an HMDSO molecule and subsequent cleave off of a methyl radical, the reaction



where $\text{Me} = \text{CH}_3$, will take place. They further pointed out that ionic reactions such as reaction (1) play an important role in their microwave plasma polymerization process. A mass spectrum of HMDSO [16] also shows the appearance of fragment ions of the form $\text{Me}_x\text{H}_{3-x}\text{Si}^+$ ($x = 1, 2, 3$).

We therefore suggest that creation of $\text{Me}_x\text{H}_{3-x}\text{Si}^+$ species either by fragmentation of HMDSO molecule ions or by reactions such as reaction (1) are responsible for the loss of SiC_xH_y species which is evident from the elemental analysis. The appearance of the SiMe_2 peak at 800 cm^{-1} in the IR spectrum may be taken as a first proof for this assumption (Figs. 2 and 3).

Figure 4 depicts AES depth profile measurements of the first 400 nm of an HMDSO/Ar film. It shows the composition of the film to be vertically homogeneous. No surface layer of different composition could be

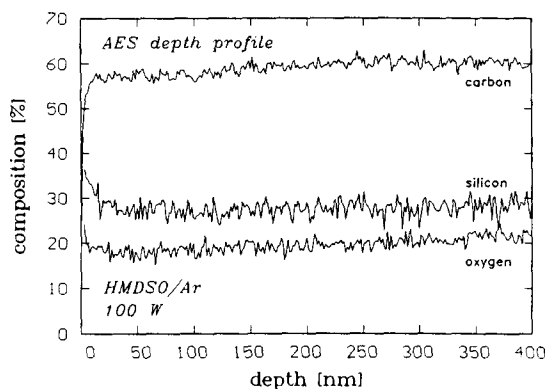


Fig. 4. AES depth profile of the first few hundred nm of a HMDSO/Ar film deposited at 100 W. The results of the elemental analysis were used to calibrated the data.

TABLE 4. Results of elemental analysis (wt.%) of polymer films obtained from the three monomers. All elements were determined independently

Monomer	Reactant	Power	C	H	Si	O	Elemental formula
HMDSO	Ar	100 W	37.2	7.6	40.0	14.8	$\text{C}_{3.33}\text{H}_{8.17}\text{Si}_{1.54}\text{O}_1$
DVTMDSO	Ar	100 W	48.9	7.4	29.1	12.7	$\text{C}_{5.16}\text{H}_{9.37}\text{Si}_{1.32}\text{O}_1$
OMCATS	Ar	100 W	31.8	6.4	39.7	19.6	$\text{C}_{2.15}\text{H}_{5.20}\text{Si}_{1.15}\text{O}_1$
OMCATS	Ar/O ₂	60 W	0.4	1.4	42.5	52.6	

Note that the sum of all elements is not exactly 100% in all cases.

detected as has been found by Wrobel *et al.* [15]. The reasons for these differences may be found in the different deposition conditions used in our work and that of Wrobel *et al.* According to these authors, additional crosslinking of the already deposited films takes place remote from the surface by energetic ions and especially photons from their microwave discharge. This results in densities of about 1.7 g cm^{-3} of the bulk polymer whereas the surface layer is considerably less dense ($\approx 0.75 \text{ g cm}^{-3}$). In the case of our 13.56 MHz plasma, the bombardment of the polymer films with these energetic particles is considerably less pronounced. Therefore, no additional crosslinking within the polymer bulk will take place. This results in more homogeneous films of constant densities of about 1 g cm^{-3} (see below).

3.1.2. DVTMDSO

The most striking difference between the IR spectra of the DVTMDSO monomer and the respective Ar/100 W polymer is the lack of any vinyl correlated peaks in the polymer spectrum (Fig. 5). This means that the vinyl groups must either be cleaved off during the polymerization process, or that they must take an active part in this process. Further differences between polymer and monomer spectra are the broadening of the ASM peak and the appearance of the SiH band as has been the case with HMDSO.

On the contrary, a comparison between the spectra of the DVTMDSO and the HMDSO polymers also yields striking differences. First of all, no peak at 1350 cm^{-1} is observed (see Fig. 3). Therefore, building of Si-CH₂-Si bridges does not play a role in the DVTMDSO polymerization process. Further, the carbon content of the DVTMDSO polymer is higher, and there are several carbon related peaks at 2925, 2855, and 1460 cm^{-1} which are not present in the spectrum of the HMDSO

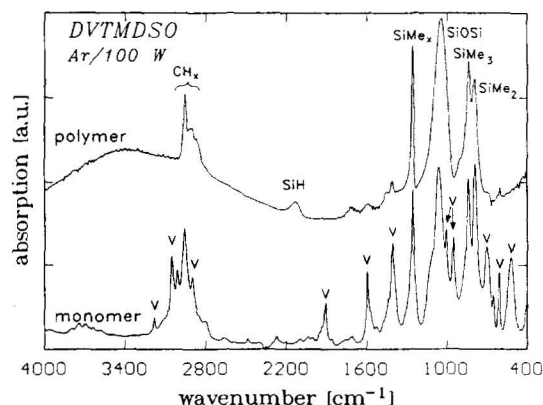


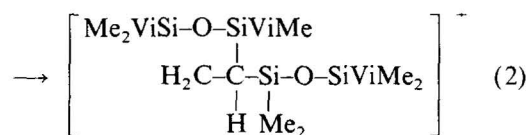
Fig. 5. FTIR transmission spectra of the DVTMDSO monomer and of a polymer film deposited at 100 W using Ar as excitation gas. The peaks in the monomer spectrum labeled V are due to the vinyl groups. For a detailed identification see Table 3.

polymer. These peaks can be attributed to free CH₂ groups (*i.e.* CH₂ groups not bonded to silicon). The higher carbon content of the DVTMDSO polymers is confirmed by the result of the elemental analysis shown in Table 4, and also by AES measurements.

The loss of vinyl bonds on the one hand, and the high carbon content and, moreover, the presence of free CH₂ groups on the other hand, lead to the conclusion that the vinyl groups are not cleaved off during the plasma polymerization of DVTMDSO but that they react by building Si-(CH₂)₄-Si groups. This reaction therefore must be an important polymerization mechanism.

Again, if this were the only mechanism the ratio of Si/O in the polymer should be 2 as in the monomer, and, as is the case with HMDSO, the elemental analysis (Table 4) shows this ratio to be lower. One possible explanation for this would again be reactions and fragmentations resulting in the creation of Me_xH_{3-x}Si⁺ species, *e.g.* according to reaction (1). However, Table 4 also shows the H/C ratio in these films to be very low thus indicating the presence of CH groups within the films (owing to interference with the CH₂ band at 2925 cm^{-1} , CH and CH₂ can hardly be distinguished in the infrared spectra).

A mass spectrum of the DVTMDSO [16] shows that cleaving of a CH₃ group is the first fragmentation process of the molecule ion. Subsequently, the following reaction may take place:



Alternatively, this reaction may also be of radical rather than ionic character. (This remark may also hold for reaction (1). In contrast, in the case of HMDSO polymerization in a microwave plasma the ionic character of reaction (1) has been proven by Wrobel *et al.* [1, 3].) In either case, reaction (2) would lead to the incorporation of CH groups which in turn would explain the low H/C ratio of the DVTMDSO films. A final proof of reaction (2), however, has not yet been performed.

A last observation concerning DVTMDSO polymers has to be mentioned. HMDSO and OMCATS films have been found to be very stable under exposure to air for several months. In contrast, in FTIR spectra of DVTMDSO films a small but distinct peak at 1750 cm^{-1} was found, the intensity of which increases with time. This peak can be assigned to C=O-groups. Aging of plasma polymer films has been correlated with the concentration of trapped free radicals within the films [1]. In contrast, Nguyen and coworkers [17] have shown that in DVTMDSO polymers the radical density

is higher than in polymers from other silico-organic monomers (without double-bonded carbon). Therefore, we suggest the reaction of trapped radicals with oxygen from the air to be the reason for the existence of this C=O peak and its increase with time. A further hint for the validity of this assumption may be seen in the fact that some of the DVTMDSO films had a yellowish appearance (see below) which can be attributed to unpaired spins within the polymers.

3.1.3. OMCATS

Comparing the infrared spectra of the OMCATS monomer and of the 100 W/Ar polymer (Fig. 6), one observes a splitting of the ASM peak to be the most prominent feature of the polymer spectrum (the splitting is even more clearly visible in Fig. 3). Further differences are the reduced carbon content and, again, the appearance of a small SiH peak. In contrast to the polymer spectra of HMDSO and DVTMDSO, there are no CH₂ correlated peaks, neither owing to Si-CH₂-Si (Fig. 3) nor owing to free CH₂.

From these observations, two conclusions can be drawn. The lack of a CH₂ correlated peak means that the carbon groups are not involved in the polymerization process. The splitting of the Si-O-Si ASM peak, however, is typical for longer siloxane chains and greater polysiloxane rings [14]. In the case of OMCATS, therefore, polymerization occurs via the formation of a network of siloxane rings and chains. Further evidence is given by the appearance of the SiMe₃ peak in the polymer spectrum (Figs. 3 and 6), while a closer examination of this spectrum [16] also reveals SiMe₂ groups to be present. Both these groups mark the chain ends and the knots of the network, respectively.

Our conclusions are also in agreement with the results of the elemental analysis (Table 4). The Si/O ratio is approximately unity as required for a siloxane network. With respect to the monomer, there is some loss

TABLE 5. Some properties of the polymer films obtained from the three monomers. The first column gives the composition of the films in at.% neglecting the hydrogen content

Monomer	Si	C	O	Refractive index	Density (g cm ⁻³)	Hardness
	(at.%)					
HMDSO	25	57	16	1.48–1.50	≈ 1	soft
DVTMDSO	18	69	13	1.50–1.52	≈ 1	soft
OMCATS	27	50	23	1.46–1.48	1.3–1.4	hard

of hydrocarbon groups, in accordance with the FTIR spectra.

3.1.4. Comparison of film properties

The composition and structure of the polymer films, and the differences between the films from the different monomers, as they have been outlined above, reflect in the various film properties. These are discussed in detail in ref. 11; in the following, we will give a brief summary (see also Table 5).

To begin with properties common to polymers from all three monomers, the films are chemically very stable against potassium hydroxide (KOH) as well as against hydrofluoric acid (HF). They are smooth, transparent (with the exception of DVTMDSO films which are sometimes yellowish as already mentioned), free of stress, and well adherent to the silicon substrates. Differences exist with respect to the refractive indices which at least in part can be attributed to the respective carbon contents of the films (Table 5).

The most important differences, however, were found in the densities and the hardness of the films. HMDSO and DVTMDSO 100 W/Ar films possess densities of about 1 g cm⁻³ and are rather soft. In contrast, the respective OMCATS films have densities between 1.3 and 1.4 g cm⁻³ and are considerably harder. This is due to the composition of the films of a siloxane ring and chain network, whereas a considerable part of the crosslinking of the HMDSO and DVTMDSO films is due to carbon related groups.

3.2. Oxygen and Ar/O₂ as excitation gas

Unlike the case of argon, reaction of the three monomers with oxygen or even oxygen/argon mixtures results in films of similar composition exhibiting an almost inorganic character as is evident from the FTIR spectra in Fig. 7 and the data of the elemental analysis shown in Table 4.

The carbon related peaks are very weak, and no SiH peak can be found. On the contrary, the ASM peak is very broad and has a shoulder at about 1150 cm⁻¹, and there are several bands owing to OH respective silanol groups which are all features of low-temperature inorganic SiO₂-like films. The broadening of the ASM peak

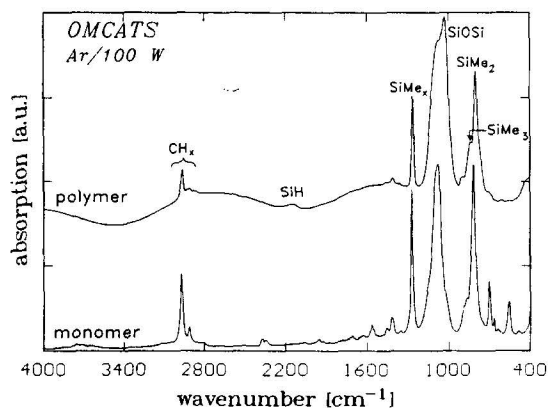


Fig. 6. FTIR transmission spectra of the OMCATS monomer and of a polymer film deposited at 100 W using Ar as excitation gas.

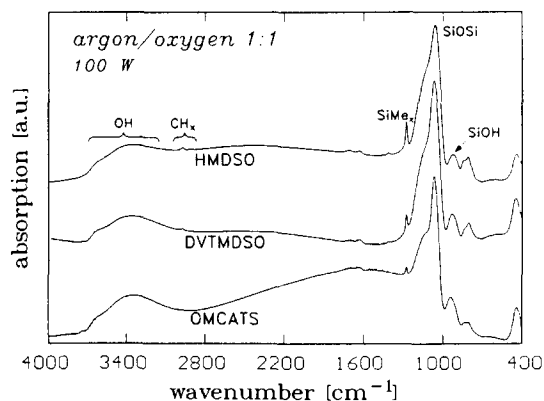


Fig. 7. FTIR spectra of films from the three monomers deposited with a 1:1 mixture of Ar and O₂. Power: HMDSO and DVTMDSO, 100 W; OMCATS, 60 W.

indicates a variety of bond lengths and angles within the films. The shoulder at 1150 cm⁻¹ has been correlated to extrinsic distortions within the Si-O network and should be due to the impurities such as carbon and silanol groups [18].

Comparing films from the three monomers, slight differences in the carbon content are found with $[C]_{\text{HMDSO}} > [C]_{\text{DVTMDSO}} > [C]_{\text{OMCATS}}$. In the case of OMCATS, this reflects the lower carbon content of the monomer itself as well as the fact that less oxygen is required to oxidize the silicon. Therefore, more oxygen is available to react with the methyl groups. The higher carbon content of the HMDSO films with respect to the DVTMDSO polymers may be due to the fact that in the presence of oxygen the vinyl groups can be more easily removed than methyl groups. However, this higher carbon content may also be attributed to the much higher growth rates of the HMDSO films ($R_{\text{HMDSO}} > R_{\text{DVTMDSO}} \approx R_{\text{OMCATS}}$).

This inorganic composition of the oxygen respective argon/oxygen polymers also reflects in their properties:

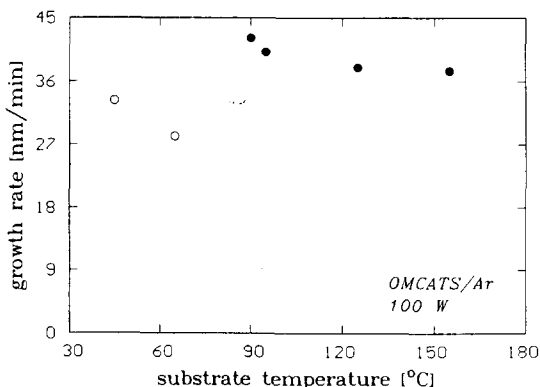


Fig. 8. Influence of the substrate temperature of the growth rates for the OMCATS/Ar process. Two sets of data for different bubbler temperatures are shown: ○, 14 °C; ●, 16.5 °C.

the densities are high (1.7–2.0 g cm⁻³), and the films are hard and scratch resistant, but also show a sometimes considerable stress. They are also not stable in the presence of either HF or KOH. For a more detailed discussion of the film properties, we again refer to ref. 11.

4. Deposition kinetics

In the following we will discuss the dependence of the growth rate of the various polymer films on important deposition parameters such as r.f. power, gas flow, and substrate temperature, in order to obtain further information on the polymerization processes.

4.1. HMDSO/Ar and OMCATS/Ar

The deposition kinetics of the HMDSO/Ar and OMCATS/Ar processes were found to be very similar. We will therefore discuss them using the OMCATS experiments as an example.

The r.f. power P and the bubbler temperature T_B were found to have the greatest influence on the growth rates. This becomes evident from the data in Figs. 8–10. Figure 8 shows that the growth rates slightly decrease with increasing substrate temperature. Desorption of film-forming precursors may be the reason for this decrease. On the contrary, the figure also shows the much greater influence of the bubbler temperature. As is evident from Fig. 9, the rates also decrease slightly with the excitation gas flow (argon flow). This is not fully understood yet, but it may simply be an effect of changing flow conditions in the reactor, since source gas and excitation gas are fed at different positions into the reactor (Fig. 1).

In Fig. 10, the growth rate R is plotted as a function of the r.f. power. Two regions can clearly be distinguished. There is a linear increase of R with P up to ≈ 100 W above which the rate saturates. This saturation

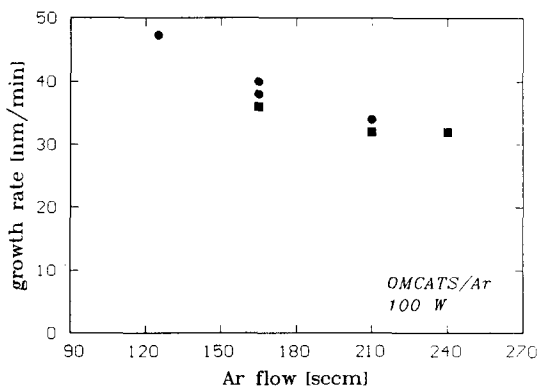


Fig. 9. Influence of the argon excitation gas flow of the growth rates for the OMCATS/Ar process. Two sets of data are shown with different positions of the throttle valve resulting in different pressures: ●, 0.32 mbar; ■, 0.49 mbar.

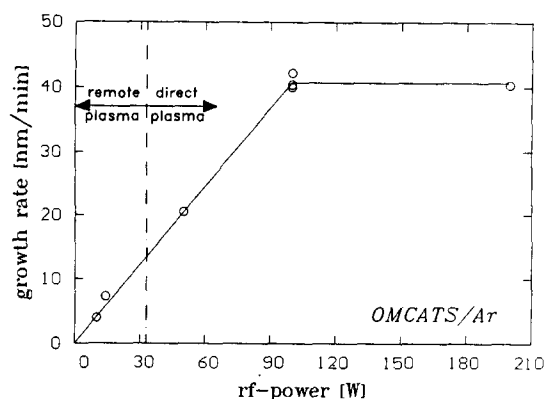


Fig. 10. Influence of the r.f. power on the growth rates for the OMCATS/Ar process. Also indicated are the ranges of the remote and the direct plasma mode, respectively.

tion can be explained by depletion of one of the reactants. The linear relationship between R and P below 100 W indicates increasing fragmentation of monomer molecules owing to an enhanced electron density n_e , since raising the r.f. power P monotonically increases n_e whereas the electron temperature is nearly unaffected by P [19]. Also from Fig. 10 it is evident that in the remote plasma mode ($P < 30$ W) only very low growth rates are obtained. It therefore seems that direct plasma dissociation of the OMCATS monomer, e.g. by electron impact, plays a prominent role in the polymerization process. The same observation also holds for HMDSO.

Figure 11 shows a section of FTIR spectra of some OMCATS films which were deposited under identical conditions apart from the varying r.f. power. It can clearly be seen that the left maximum of the split Si-O-Si ASM peak becomes more and more pronounced with increasing power. This is an indication of longer chains and respective larger rings in the polymethylsiloxane network [20] which in turn shows that with increasing power more fragmentation processes of

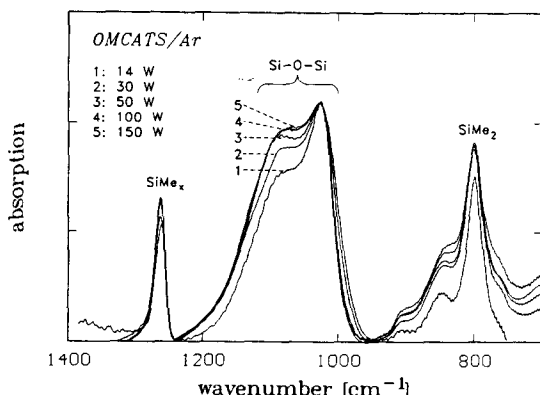


Fig. 11. Influence of the r.f. power on the form of the FTIR spectra of OMCATS/Ar films in the wavenumber range 1500–700 cm^{-1} .

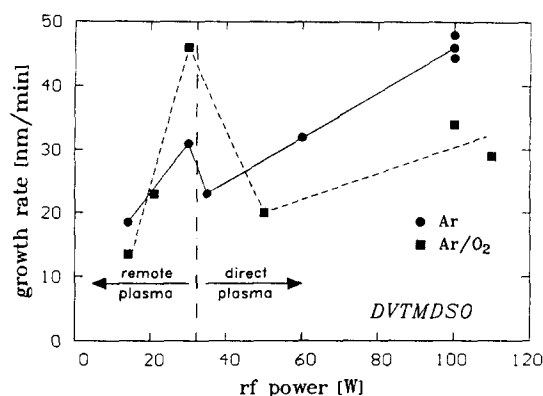


Fig. 12. Influence of the r.f. power on the growth rates for the DVTMDSO/Ar and the DVTMDSO/Ar/O₂ process. Also indicated are the ranges of the remote and the direct plasma mode, respectively.

OMCATS molecules owing to electron impact take place, in accordance with the growth rate results.

4.2. DVTMDSO/Ar and DVTMDSO/Ar/O₂

With respect to parameters such as substrate temperature, gas flows and pressure, similar dependencies were also found for DVTMDSO. There is, however, one remarkable exception. As can be seen from Fig. 12, there is a considerable deposition taking place in the remote plasma region. This behaviour was observed for argon as well as for argon/oxygen mixtures. Evidently, in the case of DVTMDSO direct plasma fragmentation of the monomer is not necessary for polymerization; reaction with either excited argon or oxygen species seems to be sufficient. At this point it is worth mentioning that DVTMDSO is the only one of the three monomers investigated which can be polymerized classically.

Increasing the power above 30 W, thereby switching from the remote to the direct plasma mode, results in sudden decrease of the growth rate which, however, increases again as the power is increased further. The reason for this drop of R is not fully understood yet. It should be mentioned, however, that this drop is also apparent if one considers the mass deposition rate R' (in $\mu\text{g cm}^{-2} \text{min}^{-1}$) rather than R . In other words, the film density does not change noticeably at this transition.

Evidently, there are two mechanisms responsible for the plasma polymerization of DVTMDSO in the remote and in the direct plasma mode. Up to now, the characterization of the remote plasma samples is not completed. Therefore, identification of these mechanisms must be postponed. However, the following observations are worth mentioning: First of all, no C=O bonds are observed in the remote samples even after storing them in air for several months, in contrast to all direct plasma samples investigated (see above). Furthermore, a comparison of the Si-O-Si ASM peaks in the FTIR spectra shows this peak to be considerably

narrower for remote plasma samples. Since the width of this peak depends on the variety of bond angles and lengths within the films this indicates that in the remote plasma case the polymers are built more regularly. Also, the carbon content is somewhat higher in the case of the remote plasma samples. At this point it may be speculated that those mechanisms which require direct plasma excitation of the DVTMDSO molecule in order to create ions or radicals, *i.e.* reactions according to reactions (1) and (2) are not taking place in the remote case. However, a final proof of this assumption in form of elemental analysis of these remote samples is still standing out.

5. Summary and conclusions

The mechanisms of plasma polymerization of HMDSO, DVTMDSO, and OMCATS have been investigated. The experimental set-up allowed the use of either a direct or remote plasma excitation. With argon as the reactant, each of the monomers shows a different polymerization pattern. With HMDSO, building of Si-CH₂-Si links plays an important role, while in the case of DVTMDSO the vinyl groups react to form Si-(CH₂)₄-Si bridges. For both monomers, however, a second mechanism must be present which is responsible for the loss of SiC_xH_y groups. In accordance with the literature, we suggest fragmentation reactions creating Me_xH_{3-x}Si⁺ species to be responsible for this loss of silicon and carbon. In the case of DVTMDSO, reactions such as reaction (2) may further be responsible for the low H/C ratio. Finally, OMCATS polymerizes via the formation of a network of siloxane chains and rings. The differences in the film composition owing to the various reaction mechanisms also reflect in the film properties with, for example, the OMCATS films being more dense and harder than the two other polymers.

With oxygen and oxygen/argon mixtures, almost inorganic films were obtained which differ only slightly from monomer to monomer. These films are hard and scratch resistant but often show considerable stress.

Plasma power and monomer flow (bubbler temperature) have been identified to be the decisive parameters determining the growth rates of the polymer films. For the HMDSO/Ar and OMCATS/Ar processes, similar power dependencies were found showing a linear relationship up to a saturation region which is due to depletion of a reactant. The linear increase is interpreted in terms of an increased monomer dissociation. In addition, the deposition rates under remote plasma conditions are very small. Finally, with higher powers the crosslinking of the films increases. These are strong hints that in the case of HMDSO and OMCATS direct plasma excitation of the monomer is an important step in the polymerization process.

In contrast, with DVTMDSO deposition was found under remote conditions with either argon or oxygen. This reflects the fact that this monomer can also be classically polymerized and that reaction with either excited argon or oxygen is sufficient to initiate polymerization. Different mechanisms seem to be responsible in the remote and the direct plasma mode, respectively. It is speculated that those processes requiring plasma excitation (e.g. ionization, reactions (1) and (2)) of the monomer are missing under remote conditions, but a final proof of this assumption still has to be carried out.

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