MECHANISMS OF PLASMA POLYMERIZATION OF DIFFERENT SILICO ORGANIC MONOMERS

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Abstract

The plasma polymerization of hexamethyl disiloxane, divinyltetramethyl disiloxane, and octamethyl cyclotetrasiloxane was investigated using either argon or oxygen as reactant. With argon, different mechanisms of polymerization were identified reflecting the respective nature of the monomers. On the other hand, with oxygen almost inorganic films were obtained irrespective of the monomer. By further comparing direct and remote plasma reaction, we conclude that in the cases of HMDSO and OMCATS direct plasma dissoziation is necessary to promote the polymerization process, whereas DVTMDSO also polymerizes under remote conditions.

1 Introduction

Silico organic plasma polymerized thin films attract increasing interest for applications in such diverse fields as optics, electronics, sensorics, and biomedicine [1]. In many cases these films have to meet a long list of requirements with respect to their properties. In order to design a film and its deposition process with respect to a special application, an increased understanding of the correlation between the monomer and the polymerization conditions used, the respective mechanisms of polymerization, and the resulting film composition and properties is required.

We therefore investigated the mechanisms of plasma polymerization of three different silico organic monomers, namely hexamethyl disiloxane (HMDSO), octamethyl cyclotetrasiloxane (OMCATS), and divinyltetramethyl disiloxane (DVTMDSO) (Table 1). Argon and oxygen were used as reactants.

momomer	formula	acronym
hexamethyl disiloxane	$(Me_3Si)_2O$	HMDSO
1,3–divinyl 1,1,3,3–tetramethyl disiloxane	$((H_2C{=}CH)Me_2Si)_2O$	DVTMDSO
octamethyl cyclotetrasiloxane	$(Me_2SiO)_4$	OMCATS

Table 1: Silico organic monomers used in our study. Me = CH_3.

In the following, we will show that with argon as reactant, different mechanisms are responsible for the formation of plasma polymer films from the three monomers. These differences in film composition and structure correspond to differences in film properties. On the other hand with oxygen inorganic films are obtained, the composition of which show only minor differences from monomer to monomer.

The main point of this report is the evaluation of the different mechanisms of polymerization. The deposition kinetics as well as the investigation of film properties will be discussed in a separate paper [2].

2 Experimental

Experimental Setup The plasma polymerization was carried out in commercial remote PECVD system (PLASMOX II, Plasmos, Munich) described in detail elsewhere [2, 3]. It consists of two chambers: A stainless steel vessel (40 cm diameter, 15 cm height) serves as reaction and deposition chamber; it is provided with a 25 cm diameter heatable substrate holder placed at its bottom. On its top there is the plasma chamber consisting of a quartz tube with a diameter of 10 cm and a height of 30 cm. Only the reactant (excitation gas) is fed into the plasma chamber whereas the monomers (source gases) are directly introduced into the reaction chamber.

The signal of a 13.56 MHz generator is coupled capacitively into the quartz tube to create the plasma. With this design, two different modes of plasma excitation can be applied: In the low rf power range (< 30 W), the plasma is confined within the plasma chamber; therefore 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 dissoziation of the monomer will play an important role (direct plasma mode). By this means it is possible to evaluate the contributions of plasma dissoziation of the monomer molecules and of their reactions with the excitation gas, respectively, to the polymerization process. (For details of the remote technique see [3, 4, 5]).

Table 2 summarizes the deposition parameters used throughout these experiments.

Film Characterization Ellipsometry (Plasmos SD 2300) and interferometry (Leitz MPV-SP) were used for thickness measurements as well as the determination of the refractive index of the films. Densities of some representive deposits were deduced from thickness and gravimetric measurements. Absorption spectra of the polymers on the silicon substrates were recorded with a FTIR spectrometer (BIORAD FT 60A) in the transmission mode. For further characterization of the film composition, elemental analysis (EA) and Auger electron spectroscopy (AES) were employed.

	HMDSO	DVTMDSO	OMCATS
bubbler temperature [°C]	-28.5	-15	16.5
monomer partial pressure [mbar]	0.014	0.004	0.004
rf power [W]	14–100		
substrate temperture [°C]	90–100		
pressure [mbar]	0.26–0.32		
carrier gas flow [sccm]	65–100		
excitation gas flow [sccm]	100–210		

Table 2: Deposition parameters used throughout our experiments.

3 Results and Discussion

3.1 Excitation with argon

As already mentioned, different mechanisms of polymerization were found for the three monomers if argon is used as excitation gas. It is therefore necessary to discuss them separately.

HMDSO Fig. 1 shows the FTIR transmission spectra of the HMDSO monomer and of a polymer film deposited with an rf power of 100 W and argon as excitation gas.

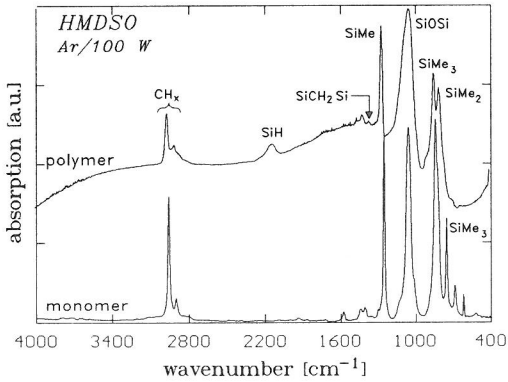

Figure 1: FTIR transmission spectra of the HMDSO monomer and of a polymer film deposited at 100 W using Ar as excitation gas. Only those peaks are labeled which are relevant to our discussion. A complete identification of the peaks is given in [2]. As references for the identifications see [6, 7]. The low wavenumber section of the polymer spectrum is shown enlarged in Fig. 2.

There are several characteristic differences between the two spectra which are due to the polymerization: In the polymer, the carbon content (with respect to the Si–O–Si bonds) is lower. On the other hand, 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}), $Si(CH_3)_2$ (800 cm^{-1}), and $Si–CH_2–Si$ (1350 cm^{-1}, see also Fig. 2). Despite its weakness, the latter (due to CH_2 scissors vibrations) is of special importance. It is usually accompanied by a much stronger band due to the CH_2 wagging mode in the 1080 to 1040 cm^{-1} region [6]. In the case of oxygen containing polymers like the HMDSO films under discussion, this CH_2 wagging peak is masked by the Si–O–Si ASM peak. However, it is found e.g. in the spectra of oxygen free hexamethyl disilazane plasma polymers [8]. 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 it is evident that the very existence of the small 1350 cm^{-1} peak proves the building of $Si–CH_2–Si$ bridges to be at least one of the polymerization mechanisms of the HMDSO/Ar process.

Monomer	Reactant	Power	C	H	Si	O	Elemental Formula
HMDSO	Ar	100 W	37.2	7.6	40.0	14.8	$C_{3.33}H_{8.17}Si_{1.54}O_1$
DVTMDSO	Ar	100 W	48.9	7.4	29.1	12.7	$C_{5.16}H_{9.37}Si_{1.32}O_1$
OMCATS	Ar	100 W	31.8	6.4	39.7	19.6	$C_{2.15}H_{5.20}Si_{1.15}O_1$
OMCATS	Ar/O_2	60 W	0.4	1.4	42.5	52.6	

Table 3: Results of elemental analysis (in %w/o) of polymer films obtained from the three monomers. All elements were determined independently. Note that the sum of all elements is not exactly 100% in all cases.

If this would be the only mechanism the ratio Si:O should be 2 (as in the monomer). However, this is not the case

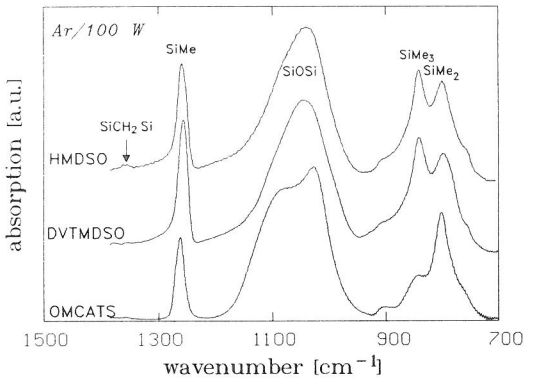

Figure 2: Comparison of the spectra of the Ar/100 W polymer films from the three momomers in the wavenumber range from 1500 – 700 cm^{-1}.

as is evident from the results of an elemental analysis of this film presented in Tab. 3. Thus there must be a second mechanism of crosslinking which is responsible for the excess loss of SiC_xH_y species.

In their work on the mechanisms of polymerization of HMDSO Wrobel and coworkers [1, 8] have proposed that after ionization of an HMDSO molecule reactions according to

$$Me_3SiOSi^+Me_2 + Me_3SiOSiMe_3 \xrightarrow{-Me_3Si^+} Me_3SiOSiMe_2OSiMe_3 \qquad (1)$$

will take place. They further pointed out that ionic reactions such as (1) play an important role in the polymerization process. A mass spectrum of HMDSO [2] also shows the appearance of fragment ions of the form $Me_xH_{3-x}Si^+$ (x=1,2,3).

We therefore suggest that creation of $Me_xH_{3-x}Si^+$ species either by fragmention of HMDSO molecule ions or by reactions like (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 prove for this assumption (Figs. 1, 2).

AES depth profile measurements show the composition of the film to be vertically homogeneous. No surface layer of different composition could be detected as has been found by Wrobel and coworkers [9].

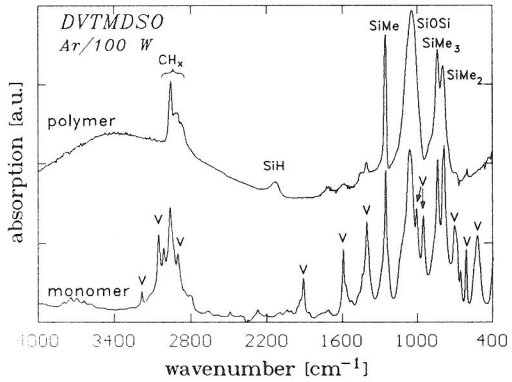

Figure 3: FTIR transmission spectra of the DVTMDSO monomer and of a polymer film deposited at 100 W using Ar as excitation gas. The peaks in the monomer spectrum labeled 'V' are due to the vinyl groups; for a detailed identification see [2, 6].

DVTMDSO The most striking difference between the IR spectra of the DVTMDSO monomer and of the respective Ar/100W polymer is the lack of any vinyl correlated peaks in the polymer spectrum (Fig. 3). This means that the vinyl groups must either be cleaved off during the polymerization process, or they must take an active part in this process. Further differences between the 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 other hand, a comparison between the spectra of the DVTMDSO and the HMDSO polymers also yield striking differences: First of all, no peak at 1350 cm^{-1} is observed (compare Fig. 2). Therefore, building of $Si–CH_2–Si$ brigdes 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, 2860, and 1460 cm^{-1} which are not present in the spectrum of the HMDSO polymer. These peaks can be attributed to 'free' CH_2 groups (i.e. CH_2 groups not bonded to silicon*). The higher carbon content of the DVTMDSO polymers is confirmed by the result of the elemental analysis shown in Tab. 3, 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 CH_2 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 $Si–(CH_2)_4–Si$ groups. This reaction therefore must be an important polymerization mechanism.

But again, if this would be the only mechanism, the ratio of Si/O in the polymer should be 2 as in the monomer, and again, as is the case with HMDSO, the elemental analysis (Tab. 3) shows this ratio to be lower. We therefore suggest the same mechanisms, i.e. reactions and fragmentations resulting in creation of $Me_xH_{3-x}Si^+$ species, to be responsible for the excess loss of silicon and carbon.

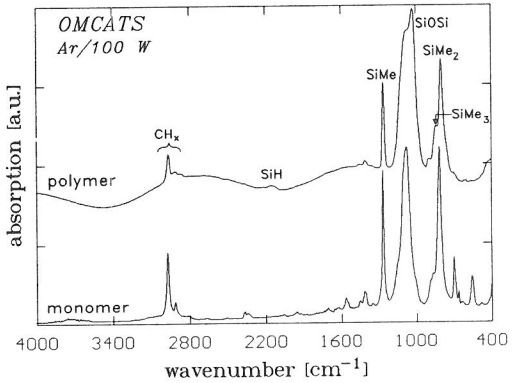

Figure 4: FTIR transmission spectra of the OMCATS monomer and of a polymer film deposited at 100 W using Ar as excitation gas.

OMCATS Comparing the infrared spectra of the OMCATS monomer and of the 100 W/Ar polymer (Fig. 4), 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. 2). 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 DVTMSO, there are no CH_2 correlated peaks, neither due to $Si–CH_2–Si$ (Fig. 2) nor due to free CH_2.

From these observations, two conclusions can be drawn. The lack of CH_2 correlated peak means that the carbon groups are not involved in the polymerization process. The splitting of the Si–O–Si ASM peak, on the other hand, is typical for longer siloxane chaines and greater polysiloxane rings [6]. 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 $SiMe_3$ peak in the polymer spectrum (Figs. 2, 4), while a closer examination of this spectrum [2] reveals also $SiMe_1$ groups to be present. These both 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 (Tab. 3). The Si/O ratio is approximately unity as required for a siloxane network. With respect to the monomer, there is some loss of hydrocarbon groups, in accordance with the FTIR spectra.

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 [2]; in the following, we will give a brief summary.

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 somewhat yellowish), free of stress, and well adherent to the silicon substrates. Differences exist with respect to the refractive indices ($n_{DVTMDSO} = 1.50 - 1.52$, $n_{HMDSO} = 1.48$, $n_{OMCATS} = 1.46 - 1.48$) which at least in part can be attributed to the respective carbon contents of the films.

*For a more detailed argumentation for this attribution see [2].

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. On the other hand, 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 Excitation with oxygen

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. 5 and the data of the elemental analysis shown in Tab. 3.

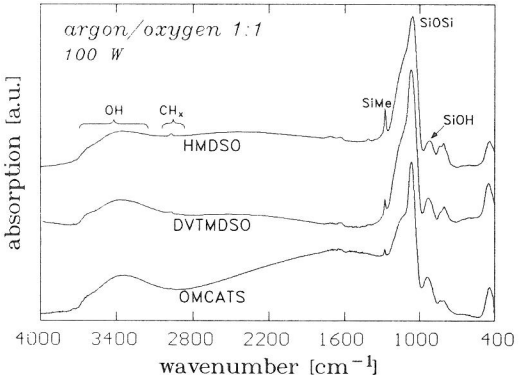

Figure 5: FTIR transmission spectra of polymer films from the three momomers deposited at 100 W using AR/O_2 as excitation gas.

The carbon related peaks are very weak, and no SiH peaks can be found. On the other hand, the ASM peak is very broad and has a shoulder at about 1150 cm^{-1}, and there are several bands due to OH respective silanol groups which are all features of low temperature inorganic SiO_2–like films. There are slight differences in the carbon content with $[C]_{HMDSO} > [C]_{DVTMDSO} > [C]_{OMCATS}$. In the case of OMCATS, this reflects the lower carbon content of the momomer 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 ($R_{HMDSO} > R_{DVTMDSO} \approx R_{OMCATS}$).

This inorganic composition of the oxygen respective argon/oxygen polymers also reflects in their properties: The densities are high (1.7 – 2.0 g/cm^3), 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 [2].

3.3 Direct and Remote Plasma

As has been discussed above, the deposition set-up used for these investigations allows the application of the direct as well as the remote plasma mode. In the former, the monomer molecules are subjected to direct plasma excitation, while in the latter they only react with a reactant which has been excited by a spatially remote plasma. By comparison of both techniques, therefore, the importance of direct plasma excitation (e.g. dissoziation, ionization by electron impact) of the monomer molecules for the overall polymerization process can be evaluated.

Our results show that one has to distinguish between HMDSO and OMCATS on the one hand, and DVTMDSO on the other hand. Using argon as reactant, with either HMDSO or OMCATS the growth rates of the polymers under remote conditions are very low ($R_{remote} \leq 0.2\ R_{direct}$) indicating that direct plasma excitation is necessary to promote the polymerization. On the other hand, with DVTMDSO $R_{remote} \geq 0.7\ R_{direct}$ can be achieved easily. At this point it is interesting to note that the divinyltetramethyl disiloxane is the only one of the three monomers used in our experiments which can be polymerized classically. Our results suggest that reaction with excited argon species is sufficient for the polymerization to occur, in contrast to HMDSO and OMCATS. Here, direct plasma dissoziation and/or ionization of the monomer molecules is required for the polymerization to occur at reasonable rates. A more detailed analysis of these aspects and of the differences of film composition and properties obtained with the remote and the direct mode, respectively, will be given in [2].

If oxygen or oxygen/argon mixtures are used, the differences are far less pronounced. All three monomers yield considerable growth rates if reacting with excited oxygen species under remote conditions. However, even in this case the ratio R_{remote}/R_{direct} is highest for DVTMDSO where it can reach unity.

4 Summary

The mechanisms of plasma polymerizations of HMDSO, DVTMDSO, and OMCATS have been investigated. The experimental setup allowed the use of either a direct or remote plasma excitation. With argon as reactant, each of the monomers shows a different polymerization pattern: With HMDSO, building of Si–CH_2–Si links plays an important role, while in the case of DVTMDSO the vinyl groups react to form Si–$(CH_2)_4$–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 literature, we suggest fragmentation reactions creating $Me_xH_{3-x}Si^+$ species to be responsible for this loss of silicon and carbon. Finally, OMCATS polymerizes via the formation of a network of siloxane chains and rings. The differences in the film composition due to the various reaction mechanisms also reflect in the film properties with e.g. 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 sligthy from monomer to monomer. These films are e.g. hard and scratch resistance but often show considerable stress.

Comparing the remote reaction with excited argon and the direct plasma excitation, our results show only DVTMDSO to react considerably under remote conditions thereby reflecting the fact that this monomer can also be classically polymerized. In the case of HMDSO and OMCATS direct plasma excitation of the monomer was recognized as an important step in the polymerization process.

Acknowledgement

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