INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS

J. Phys. D: Appl. Phys. **37** (2004) 588–594 PII: S0022-3727(04)66588-0

Fourier transform infrared spectroscopy study of molecular structure formation in thin films during hexamethyldisiloxane decomposition in low pressure rf discharge

K Li, O Gabriel and J Meichsner

Institute of Physics, University of Greifswald, Domstr 10A, D-17487 Greifswald, Germany

E-mail: li@physik.uni-greifswald.de, onnog@web.de and meichsner@physik.uni-greifswald.de

Received 28 July 2003
Published 28 January 2004
Online at stacks.iop.org/JPhysD/37/588 (DOI: 10.1088/0022-3727/37/4/010)

Abstract
The growth of plasma deposited organic films in general is non-homogeneous, i.e. the films can consist of several layers: substrate–film interface and cross-linked bulk plasma polymer. The fourier transform infrared spectroscopy study shows evidence for a substrate–film interface layer that appears to be formed during a gas conversion in a discharge. The reflection–absorption spectroscopy and evanescent wave spectroscopy techniques have been used to analyse the evolution of molecular structure of the films growing in hexamethyldisiloxane (HMDSO) plasmas of a low pressure capacitive rf (13.56 MHz) discharge. The pulsed operation mode of the rf discharge was used in order to provide successive steps of the HMDSO plasma–chemical conversion into stable neutral products, which were monitored by mass spectrometry. The HMDSO conversion exerts influences on the film deposition resulting in a gradient in the molecular structure of the growing films. The comparison of the film growth on substrates at floating and rf self-bias potentials shows that ions control the deposition kinetics and influence the molecular structure of films.

1. Introduction

Thin films obtained by plasma-assisted deposition of organosiloxane compounds have attracted great interest for a variety of applications [1]. The safety, low cost, and physical and chemical properties count for advantages of organosiloxanes over other Si-containing monomers. Hexamethyldisiloxane (HMDSO; $(CH_3)_3Si–O–Si(CH_3)_3$) is one of the most utilized organosiloxane feed gases. The deposition in HMDSO-containing plasmas has been intensively investigated in numerous studies that cover plasma diagnostics [2–7] as well as film characterization [1, 3, 8–11]. However, the plasma chemistry as well as the plasma–surface interaction in such plasmas are not well understood. In addition to an understanding of the basics of reactive plasmas, a comprehension of the film growth mechanism is required for optimization of the film quality and control of the deposition process. Structural and elemental analyses of plasma deposited films allow us to clear up the main features of film formation. Moreover, film characterization provides the information on structure–property correlations for deposits prepared at appropriate process conditions.

Electron microscopy analysis showed that the deposition in HMDSO low pressure rf plasmas on substrates with a porous surface results in the formation of films with a morphology demonstrating spherical or hemispherical structures [12]. An analogous morphology can be achieved by deposition at conditions of powder formation. The particles formed due

© 2004 IOP Publishing Ltd Printed in the UK

to oligomerization reactions in the gas phase are incorporated in a growing film [13].

In general, plasma polymers possess a stratified macrostructure: a bulk cross-linked part and top oligomeric or oxidized layer [8, 14]. Moreover, Poll *et al* [15] have evidenced a substrate–film interface layer that has a composition different from that of bulk plasma polymer film. The structural units of plasma polymerized HMDSO films were analysed by various methods, e.g. Fourier transform infrared spectroscopy (FTIR) [16] and pyrolysis/gas chromatography [8, 17], and it was found that the macromolecular chains are linear. The process condition set allow us to produce films with molecular structure and chemical composition of different types: either organic plasma polymers with a monomer-like structure, i.e. with high content of organic constituent or inorganic SiO_x-like coatings. Films rich in organic constituent can be obtained in a HMDSO plasma at conditions of low power input. High oxygen dilution of the HMDSO feed results in deposition of inorganic SiO_x films.

Most of the studies have dealt with *ex situ* investigation of structure and composition of finished films. Recently developed techniques enable *in situ* film characterization [18–22], making it possible to study the evolution of molecular structure with process time. In particular, the modern techniques of FTIR represent powerful tools for *in situ* structure analysis. Complemented by additional diagnostic methods, like x-ray photoelectron spectroscopy, FTIR spectroscopy can give a detailed picture of the film formation.

This paper is devoted to a FTIR spectroscopy study of the evolution of film structure during the HMDSO plasma–chemical conversion in a low pressure rf discharge. To clarify the influence of ion bombardment on the growth of plasma polymers (deposition rate and molecular structure), the film deposition was investigated on substrates placed on a driven electrode as well as in bulk plasma of an asymmetrical capacitive rf discharge.

The experimental set-up for film deposition and the operation procedure are described in section 2. This section covers the diagnostic techniques and thin film characterization tools also. Results of the HMDSO conversion are presented in section 3. The influence of process parameters on the HMDSO decomposition was considered with the help of a composite process parameter similar to that one introduced by Yasuda [23]. Section 4 covers the results of thin film characterization. In particular, the evolution of infrared (IR) absorption spectra of growing films is presented. The conclusions resulting from the study are summarized in the final section.

2. Experiment

The experimental arrangement is illustrated in figure 1. HMDSO (Sigma-Aldrich Chemical Co., Germany) and oxygen were supplied to the chamber from the side feed lines. The flow rates of the gases were regulated by MKS mass flow controllers that were managed by a 147B multi-channel mass flow/pressure programmer (MKS, USA). The total pressure was maintained by means of a 652 throttle valve controller (MKS, USA) connected to the programmer. The discharge was powered by an rf (13.56 MHz) ACG-5 generator (ENI, USA) coupled to the driven electrode by a fully tunable π-type matching network. The asymmetrical discharge was maintained between the substrate-carrying driven electrode (8.5 cm in diameter) and the grounded wall of the cylindrical vacuum chamber with a volume of 20 litre.

The experiments were performed by pulsed plasma operation. The chamber was pumped down to background pressure ($p < 0.01$ Pa), and every time a fresh portion of the process gas was introduced before each plasma pulse. Then the discharge was ignited for a given pulse duration, τ_{plasma}, at the conditions fixed in the accumulation series. Typical values of the process parameters used in the experiments are as follows: total pressure, 10–100 Pa; gas flow rate, 1–20 sccm; power, 10–200 W. The IR absorption spectra were taken after every plasma pulse or a set of such pulses, whereas the mass spectra were recorded for the continuous wave mode.

The neutral species in the gas phase were monitored by means of an EQP 300 mass/energy analyser (Hiden Analytical,

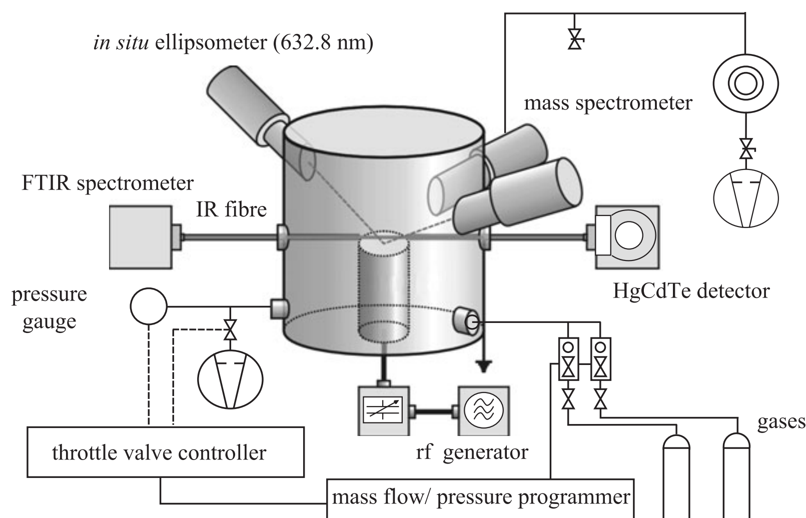

Figure 1. Schematic diagram of experimental set-up.

UK). The species were allowed to effuse from the plasma to the quadrupole mass spectrometer through an orifice of 100 μm diameter that was situated at a distance of about 20 cm outside the active plasma zone. The ions were formed from the neutral particles within the ion source, which is a dual filament electron impact source. The electron energy was 70 eV. The ion transfer optics focused ions onto the input of the 45° sector field energy analyser and then led them to the quadrupole mass filter. The ion beam was registered by a continuous dynode electron multiplier. The intensities of 15 chosen species were simultaneously recorded. The integrating time of 100 ms used for each detected fragment ion allowed us to follow the plasma–chemical conversion with a 1.5 s time step from the moment of discharge ignition up to the time when the plasma composition attains a steady state.

The evolution of the molecular structure of the films growing on the substrates at floating potential and on the driven electrode was analysed by means of FTIR spectroscopic techniques: infrared reflection absorption spectroscopy (IRRAS) and infrared evanescent wave spectroscopy (IREWS). FTIR evanescent wave spectroscopy allowed us to follow the evolution of the molecular structure of the films deposited on the active part of the chalcogenide (AsSeTe) optical fibre, which served as a waveguide and as an internal reflection element [22]. The IR transparent fibre was guided through the plasma bulk. The fibre surface was under the floating potential. Because of the very small diameter of the fibre core, 250 μm, a low distortion of plasma was assured. The IRRAS technique was used for *ex situ* structure analysis of the films formed on the driven rf electrode. These films were deposited in the following way. Si substrates, placed on the driven electrode, were covered by a screen plate. The discharge was ignited for a time up to the moment when a plasma composition attains a steady state, 240 s at the typical process parameters and reactor geometry chosen here. Then, the screen plate was removed and a substrate was coated for 10 s.

The rates of film deposition on the driven electrode were *in situ* measured using an SD2200 ellipsometer (PLASMOS GmbH, Germany) at 632.8 nm wavelength. The rate of film deposition under floating potential was derived from deposition experiments using Si substrates (1.5 cm $\times$ 1.5 cm). The Si substrate was placed in the bulk plasma at a distance of about 2 cm from the driven electrode. These films were *ex situ* analysed by a S2000 spectral (300–800 nm) ellipsometer (Rudolph Technologies, USA).

3. HMDSO conversion in stable products

3.1. HMDSO decomposition in molecules

The electron impact mass spectra of HMDSO vapour as well as HMDSO-containing plasmas have been already investigated in detail [2, 4, 24–26]. The signal from the parent ion at 162 m/z has a very low intensity. The dominant peak at 147 m/z is ascribed to the monomer molecule since this fragment ion is the direct product of cleavage of the methyl group from the HMDSO molecule (162 u). Because of the isotope presence (^{29}Si and ^{30}Si), there are two additional peaks at 148 m/z and 149 m/z with relative intensities of 16% and 9%, respectively.

A comparison of the mass spectra recorded before and after discharge ignition revealed a strong fragmentation of the HMDSO molecules in the plasma at the chosen process conditions. The intensity of the peak at 147 m/z was drastically reduced, while the signals of low molecular weight compounds became high. One should notice considerable intensities of atomic and molecular hydrogen mass signals. The fragment ion with 15 m/z is formed mainly from methane and organosilicon compounds as a result of dissociative ionization in the ion source. The orifice was far from the plasma zone, and therefore the methyl radicals formed in the plasma did not add significantly to the peak at 15 m/z. The electron impact ionization cross-section of CH_3^+ formation from ethane, C_2H_6, at 70 eV (0.5 $\times$ 10^{-17} cm^2) [27] is nearly one order lower than that from methane (0.38 $\times$ 10^{-16} cm^2) [27] or HMDSO (0.35 $\times$ 10^{-16} cm^2) [26]. Hence, the contribution of ethane in the peak at 15 m/z was negligible. At a high discharge power, when monomer molecules as well as high molecular weight organosilicon compounds are strongly decomposed in the plasma, methane can be considered as the main source for the detected signal at 15 m/z only. The 15 m/z and 16 m/z ions behaved in the same manner with variation of process parameters, which supports the thesis done earlier.

Methyl radicals, formed as a result of cleavage from the HMDSO and organosilicon molecules, recombine readily in the plasma zone, giving the stable ethane molecules. The rate coefficient for this reaction is equal to (3.8–5) $\times$ 10^{-11} cm^3 mol^{-1} s^{-1} [28], compared with 2.1 $\times$ 10^{-12} cm^3 mol^{-1} s^{-1} of the alternative reaction involving methyl radical and atomic hydrogen and leading to the formation of methane. The appropriate signals of the detected fragment ions from ethane molecules appear at 30, 28, and 26 m/z [29]. Indeed, the last two peaks are also due to the fragment ions of ethene and acetylene at 28 m/z and 26 m/z, respectively. A high content of ethane and methane molecules, up to 10^{15} cm^{-3}, was found by IR tuneable diode laser absorption spectroscopy at the process conditions utilized in this work [7].

The time evolution of mass spectra illustrates the HMDSO conversion in the discharge chamber (see figure 2). The HMDSO content decreased continuously after the discharge ignition, while intermediate organosilicon molecules, hydrocarbons, and hydrogen were formed in the gas phase with the

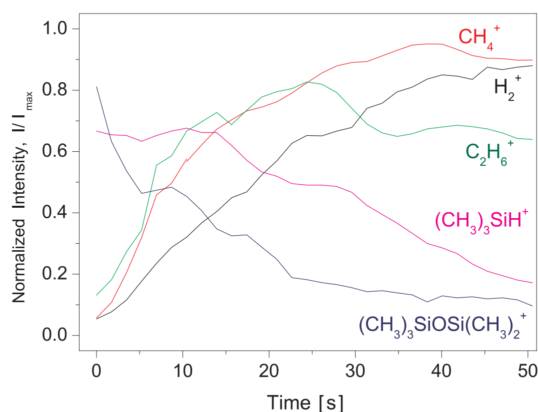

Figure 2. Time evolution of chosen positive fragment ions related to stable molecules in the reactor. Process conditions: 130 W, 15 Pa, 5 sccm HMDSO.

process time. In the case of the system without gas flow, the HMDSO molecules are fragmented completely up to molecular hydrogen and light weight hydrocarbons. The conversion in the system with the gas flow leads to moderate fragmentation of the HMDSO molecules and is characterized by the constant gas phase composition at the steady state. The variation of the plasma-on time allow us to set the appropriate degree of dissociation of HMDSO. Thus, the use of a pulsed rf discharge enables one to deposit plasma polymer films at every stage of the HMDSO plasma–chemical conversion.

3.2. Influence of process parameters on HMDSO decomposition and film deposition rates

The HMDSO decomposition can be characterized by the following parameters: conversion time and fragmentation rate. The HMDSO conversion time, τ_{conv}, was defined as the time of the exponential fall of the measured count rate $(I_0 - I)$ of the 147 m/z fragment ion; I_0 is the count rate measured without discharge and I is the count rate measured with discharge. The fragmentation rate was defined consequently as the ratio, $(I_0-I)/\tau_{conv}$. The decomposition of the monomer is a function of the process parameters (power, pressure, etc). The influence of the external process parameters on the conversion time and the fragmentation rate can be described by a composite process parameter, ϕ, analogous to the one introduced by Yasuda [23]. The composite process parameter is given by

$$\phi = \frac{WkT}{pMf},$$

where W is the discharge power, k is the Boltzmann constant, T is the gas temperature (300 K), p is the total gas pressure, M is the monomer molecule mass, and f is the gas flow rate. The conversion time of the 147 m/z fragment ion diminished with an increase in the composite parameter and reached the minimum value at a value of the parameter ϕ of about 10^{12} J kg^{-1}, while the fragmentation rate attained the maximum value (see figure 3). The value of about 10^{12} J kg^{-1} can be designated as a critical value, ϕ_C, which characterizes the minimum input energy for the strongest conversion of the HMDSO molecules for a given deposition process. The mass spectrometric measurements revealed that the count rates of the fragment ions $(CH_3)_4Si_2OH^+$ (133 m/z), $(CH_3)_2SiOH^+$ (75 m/z), $(CH_3)_3SiH^+$ (74 m/z), $(CH_3)_3Si^+$ (73 m/z), $(CH_3)SiH_2^+$, and $SiOH^+$ (45 m/z) attained the maximum at ϕ_C. The oxygen admixture results in an enhanced HMDSO fragmentation (see figure 4).

The dependence of the fragmentation rate on the parameter ϕ allows one to mark out two distinct regimes: low power input and high power input. Both regimes characterize also the influence of power input on the deposition rate in a steady state. When the power input is low, the deposition rate increases strongly with the parameter ϕ due to rising fragmentation of HMDSO molecules and intensive formation of the active species. There is a slight dependence of deposition rate on power input due to a complete fragmentation of HMDSO molecules in the second regime. Figure 5 shows the dependence of the rate of film deposition on the Si wafer placed on the driven electrode, measured in a steady state, on the composite process parameter. The curves represent the variations of a single process parameter: power, pressure, or gas flow rate. Here, the composite parameter is used for description of the surface process in contrast with the study of the HMDSO conversion where it was applied to the gas phase.

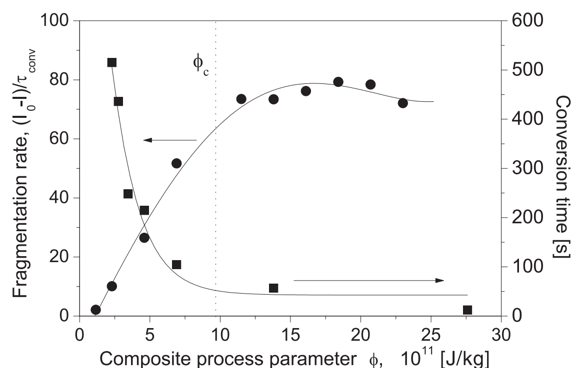

Figure 3. Fragmentation rate (●) and conversion time (■) in dependence on the composite process parameter, ϕ.

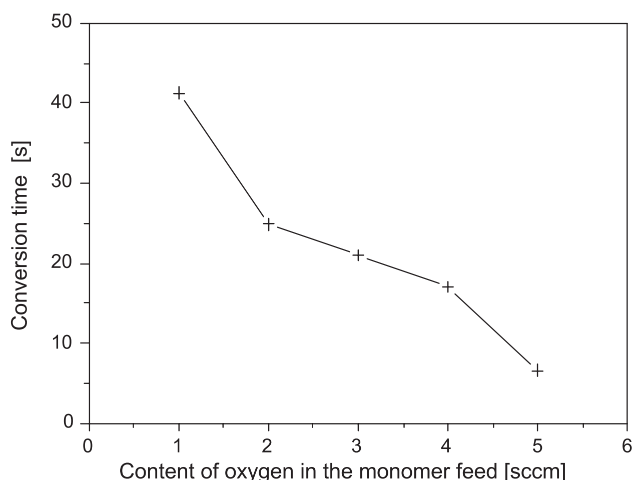

Figure 4. Influence of the oxygen content in the gas feed on the HMDSO conversion time. Process conditions: 15 Pa total pressure, 130 W discharge power, 6 sccm total flow rate.

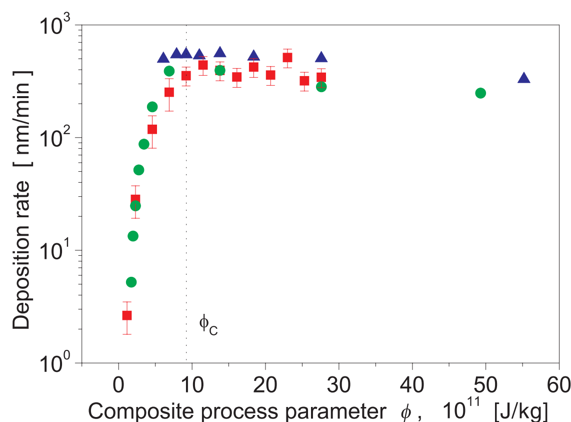

Figure 5. The composite process parameter, ϕ, dependence of the rate of film deposition in the HMDSO plasma obtained as a result of (■) power variation (5–120 W, 10 Pa, 4 sccm), (●) pressure variation (3–80 Pa, 60 W, 4 sccm), and (▲) HMDSO flow rate variation (0.5–9 sccm, 60 W, 10 Pa).

4. Formation of film structure

For film characterization, the deposition was carried out under the following plasma process conditions that are appropriate to the regime of high power input at a steady state:

(a) 15 Pa total pressure, 130 W power, and 5 sccm HMDSO gas flow rate,
(b) 15 Pa total pressure, 130 W power, 3 sccm HMDSO, and 17 sccm O_2 gas flow rates.

The different plasma-on times allow us to set the appropriate degree of HMDSO dissociation (see figure 6). Thus, the IR absorption spectra accumulated at the different plasma-on times illustrate the evolution of molecular structure of the growing films. The composition of the films analysed here is a thickness average over the film composition from discharge ignition during the whole plasma pulse period. For FTIR measurements, the films were created by depositing stacks of initial layers using plasma pulses of 1 s, 5 s, and 10 s. Only the first layer is affected by the substrate, and all of the subsequent layers are deposited on preceding layers. The sensitivity of the film structure to the substrate was not measured by FTIR techniques. It is assumed that the molecular structure of the first layer depends only on the plasma composition. Figures 7(*a*), (*b*) and 8(*a*), (*b*) show absorption spectra of films deposited in HMDSO and HMDSO/O_2 plasmas on the IR fibre under floating potential and on the driven electrode. The corresponding deposition rates are included in the figures. The absorption spectra drawn on the figures correspond to films deposited for equal total deposition times. The total deposition time of the films, the spectra of which are shown in figure 7(*a*), was equal to 50 s, while the total deposition time for the films represented in figures 7(*b*) and 8(*a*), (*b*) was 10 s. Therefore, the number of deposited layers is equal to the ratio of total deposition time to plasma pulse duration. Structural analysis of samples grown in a steady state continuous discharge was performed only for films deposited on the driven electrode.

The general assignment of the absorption lines from the molecular groups of interest is summarized in table 1. The IR spectra of plasma polymerized films were interpreted with use of the vibrational spectrum of HMDSO, which is well known [30, 31].

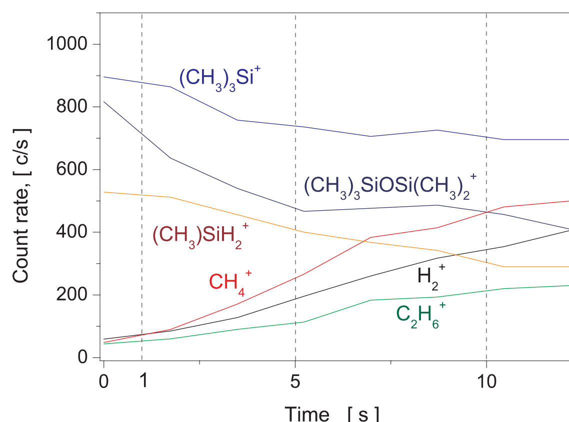

Figure 6. The gas conversion in the HMDSO rf plasma during the first 10 s when the IR absorption spectra of growing films were accumulated. Process conditions: 15 Pa total pressure, 130 W discharge power, 5 sccm HMDSO flow rate.

The deposition rates in pure HMDSO plasma on the fibre are relatively low, up to 70 nm min^{-1}. However, a small variation of the plasma–chemical conversion of the monomer results in a remarkable change in the spectrum. The intensities of the absorption lines due to vibrations of an Si–O bond in siloxane groups and methyl vibrations in methylsilane groups decrease with plasma pulse duration. This is consistent with the formation of denser films.

The high molecular weight species formed at low dissociation grades compose a monomer-like structure of plasma polymer with a relative high content of the –(CH_3) groups. Free internal rotation about an Si–O bond in the siloxane group is thereby sustained in such films, which results in the higher extinction coefficient and, hence, in the stronger absorption of the appropriate bands (1100–1000 cm^{-1}) in the spectra of films synthesized at shorter plasma pulses.

Symmetric deformation vibrations of methyl groups in Si–$(CH_3)_3$ cause an asymmetric broad band around 1256 cm^{-1} that consists of two components of unequal intensity. The presence of this group indicates a low dissociation grade of the monomer in the plasma bulk at short plasma pulses.

The molecular structure of the films deposited in an O_2/HMDSO plasma at very short plasma pulses ($\tau_{plasma} < 1$ s) is similar to that of the films obtained in the pure HMDSO plasma (see figures 7(*a*) and (*b*)). The acceleration of the film deposition on the fibre can be induced by surface activation by oxygen radicals and ions as well as by enhanced HMDSO conversion.

Despite the absorption in the region of 1020–1010 cm^{-1} being associated with cyclic siloxane trimers, their presence in plasma polymerized HMDSO films is excluded. Wrobel *et al* [8, 17] analysed the structure of plasma polymerized siloxanes by means of pyrolysis/gas chromotography and mass spectrometry and found that plasma polymerization of linear siloxanes yields only linear oligomers in the volatile fraction extracted from a film. Despite the high organic content due to weak monomer fragmentation, the plasma polymer grown on the fibre does not contain disilymethylene, Si–CH_2–Si, and disilyethylene, Si–CH_2–CH_2–Si, groups which have been detected in the deposits formed on the electrodes [8, 32]. The band due to their wagging vibrations at 1030 cm^{-1} laps over the Si–O–Si band and does not permit us to identify the presence of the corresponding groups. However, the absorption line at 1350 cm^{-1} due to –CH_2– scissoring vibrations is absent in the spectra of the PP HMDSO films. The absorption of methyl groups, 2900–2800 cm^{-1}, is small.

The growth of plasma polymer under the floating potential is unlike that of the films deposited under the rf potential due to stronger ion bombardment of the substrate and growing film on the rf electrode. The results support the thesis that the growth of the plasma polymer goes through the active centres that are formed on the surface due to the influence of energetic ions. The interaction of energetic ions with growing chains of plasma polymer film can result in free macroradicals formed on the surface. The dependence of the deposition rate on the plasma pulse duration shows a non-linear character. Plasma etching reduces the rate of film growth. The etching becomes intensive in the O_2/HMDSO plasma in the case of long plasma pulse durations. The films formed on the driven electrode in the HMDSO plasma show the following features

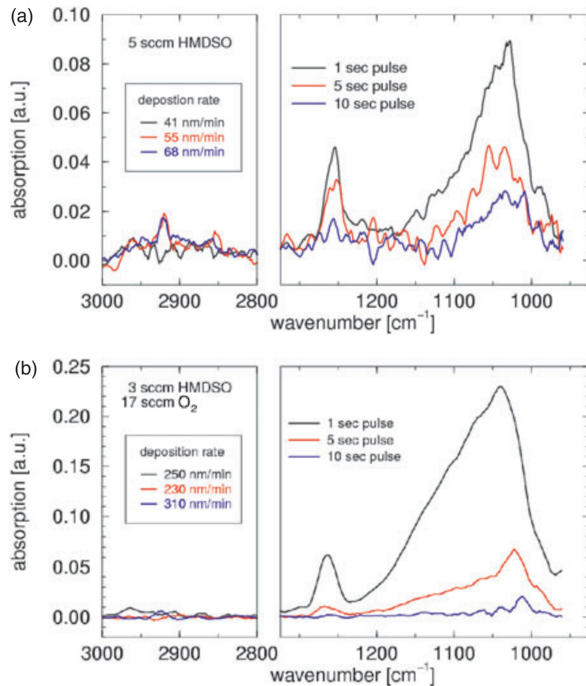

Figure 7. The FTIR absorption spectra of the films deposited on the fibre in the bulk plasma: (*a*) in the HMDSO plasma (5 sccm); (*b*) in the HMDSO/O_2 plasma (3 sccm/17 sccm). Process conditions: 15 Pa, 130 W. The absorption bands in the range 2980–2850 cm^{-1} are ascribed to CH_3 groups; 1260 cm^{-1} to $Si(CH_3)$; 1200–1000 cm^{-1} to SiO_x and Si–O–Si groups.

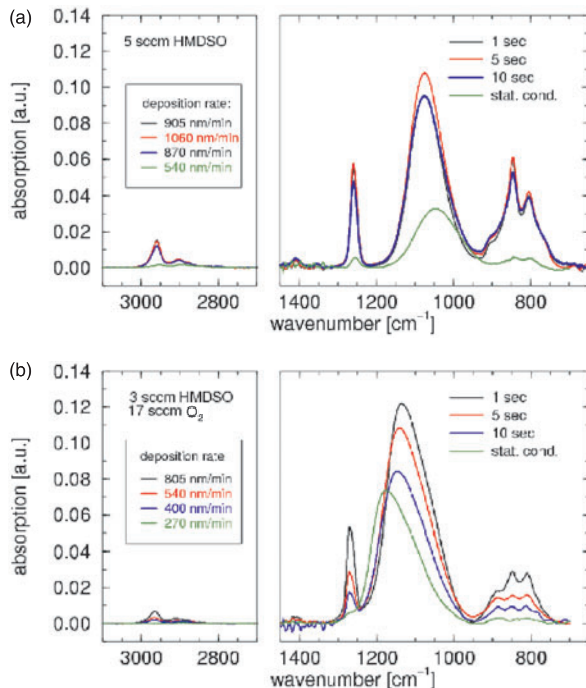

Figure 8. The FTIR absorption spectra of the films deposited on the driven electrode: (*a*) in the HMDSO plasma (5 sccm); (*b*) in the HMDSO/O_2 plasma (3 sccm/17 sccm). Process conditions: 15 Pa, 130 W. The lines 'Stat. cond.' correspond to IR absorption spectra of the films grown in a steady state of a continuous discharge. The absorption bands in the range 2980–2850 cm^{-1} are ascribed to CH_3 groups; 1260 cm^{-1} to $Si(CH_3)$; 1200–1000 cm^{-1} to SiO_x and Si–O–Si groups.

Table 1. The general assignment of the IR absorption bands to the molecular groups of interest in plasma polymerized HMDSO films [30–32, 34].

Wavenumber (cm^{-1})	Assignment
2980–2850	CH_3, CH_2
1260	Si–(CH_3)
1200–1000	SiO_x, Si–O–Si
900–750	CH_3, CH_2

in the IR absorption spectra. The absorption line due to Si–O stretching vibration does not have an explicit asymmetric form with the main peak at 1070 cm^{-1} and the shoulder at 1037 cm^{-1} (see figure 8(*a*)). There is a wide absorption line that is in the range of 1072–1043 cm^{-1}, compare figures 7(*a*) and 8(*a*). The line position depends on the molecular group containing the Si–O bond. Linear small-chain siloxanes tend to absorb at about 1050 cm^{-1} (HMDSO—at 1060 cm^{-1}). This line broadens gradually with increasing molecular weight: long-chain polymers have a broad, strong band with maximum at 1085 and 1025 cm^{-1} [33, 34]. The position of the line centre is shifted from 1072 to 1043 cm^{-1} with the plasma pulse duration while the full width at half height (FWHH) increases. These alterations in the IR absorption spectrum are explained by changes in film density, molecular environment of the siloxane group, and cross-linking structure. Therefore, a film deposited at a longer plasma pulse duration should have a higher mass density and more cross-linked structure. The molecular structure is formed mainly from the species of monomer-like structure $(CH_3)_{x=1-3}$–Si–O–Si–$(CH_3)_{y=1-3}$. Thus, the analysed films can be considered to be a type of methylpolysiloxane.

The films deposited in an O_2/HMDSO plasma at the driven electrode show the absorption lines shifted to shorter wavelengths (see figure 8(*b*)). This region is characteristic for Si–O vibrations in molecular groups as in a-SiO_2 films [35]. The formation of SiO_x-like films is evidently seen from data of XPS analysis of the chosen samples (see table 2).

5. Conclusions

The formation of molecular structure in thin films during the HMDSO plasma–chemical conversion in a low pressure rf discharge was studied by various techniques of FTIR spectroscopy (IRRAS and IREWS). The rate of film deposition was measured by ellipsometry. The plasma polymer films were deposited at the consequent stages of HMDSO decomposition. The results of the analysis evidence that the molecular structure of the growing film is not homogeneous. At various steps of the HMDSO conversion, different precursors form the growing film, which assures a gradient in molecular structure. A low grade of the HMDSO fragmentation (initial steps of the conversion) results in a monomer-like (i.e. with a high content of organic constituent) molecular structure of the films deposited both on the driven electrode and on the substrates at floating potential. The intensive HMDSO fragmentation at long plasma-on times results in the growth of dense films with slightly lower content of organic constituent.

A mass spectrometric study of the stable neutral gaseous products shows that the HMDSO conversion can be controlled

Table 2. Si, O, and C content in percentage (%) in the films deposited on substrates in bulk plasma and on a driven electrode. Process conditions: 15 Pa, 130 W, 5 sccm HMDSO or 3 sccm HMDSO/17 sccm O_2.

	In bulk plasma						On driven electrode					
	HMDSO			HMDSO/O_2			HMDSO			HMDSO/O_2		
Plasma-on time (s)	Si	O	C	Si	O	C	Si	O	C	Si	O	C
1	25	24	51	20	43	37	24	29	47	21	47	32
10	22	24	54	22	50	28						
240							24	31	45	22	58	20

by the power input and O_2 admixture. For a given plasma reactor, a critical value of the composite process parameter, ϕ, was found, at which the HMDSO fragmentation rate and the rate of film deposition attain the maximum. The critical value is equal to 10^{12} J kg^{-1} at the process conditions used in this work.

The rate of film deposition on the substrates at floating potential increases with the plasma pulse time. The decrease in the rate of film deposition on the driven electrode with the plasma pulse time appears to be caused by plasma etching due to intensive ion bombardment. The O_2 admixture not only accelerates the HMDSO fragmentation but also influences the film formation. The rate of deposition at floating potential increases, e.g. 55 nm min^{-1} in HMDSO plasma vs 230 nm min^{-1} in O_2/HMDSO plasma. At the same time, the deposition rate at rf potential in the O_2/HMDSO plasma, e.g. 540 nm min^{-1}, is lower than that in the pure HMDSO plasma, e.g. 1060 nm min^{-1}, mainly due to etching and oxidation processes. The latter contributes also to the formation of the SiO_x-like molecular structure of the films.

Acknowledgment

This work was supported by Federal Ministry of Education and Research of Germany Grant No 13N8051. The authors thank Mr V Vartolomei, who performed XPS measurements.

References

[1] Wrobel A M and Wertheimer M R 1990 Plasma-polymerized organosilicones and organometallics *Plasma Deposition, Treatment, and Etching of Polymers* ed R d'Agostino (London: Academic) p 163
[2] Schmidt M, Foest R, Basner R and Hannemann M 1994 *Acta Phys. Universitatis Comenianae* **35** (N2) 217–27
[3] Lamendola R, d'Agostino R and Fracassi F 1997 *Plasmas Polym.* **2** (N3) 147–64
[4] Alexander M R, Jones F R and Short R D 1997 *Plasmas Polym.* **2** (N4) 277–300
[5] Segui Y and Raynaud P 1997 Plasma diagnostic by infrared absorption spectroscopy *Plasma Processing of Polymers* ed R d'Agostino *et al NATO ASI Series, Series E: Appl. Sci.* vol 346 (Dordrecht: Kluwer) pp 81–100
[6] Schwabedissen A, Soll Ch, Brockhaus A and Engemann J 1999 *Plasma Sources Sci. Technol.* **8** (N3) 440–7
[7] Röpcke J, Rivalde G, Osiac M, Li K and Meichsner J 2002 *Plasma Chem. Plasma Proc.* **22** (N1) 139–59
[8] Wrobel A M, Kryszewski M and Gazicki M 1983 *J. Macromol. Sci. Chem.* A **20** (N5 & 6) 583–618
[9] Zuri L, Silverstein M S and Narkis M 1996 *J. Appl. Polym. Sci.* **62** 2147–54
[10] Alexander M R, Short R D, Jones F R, Stollenwerk M, Zabold J and Michaeli W 1996 *J. Mater. Sci.* **31** 1879–85
[11] van Ooij W J, Eufinger S and Guo Sh 1997 *Plasma Chem. Plasma Proc.* **17** (N2) 123–54
[12] Li K and Meichsner J 1999 *Surf. Coat. Technol.* **116–119** 841–7
[13] Courteille C, Magni D, Deschenaux C, Howling A A and Hollenstein C 1998 *Proc. 41st Annual Tech. Conf. Soc. Vac. Coaters (Albuquerque, 1998)* pp 327–32
[14] Wrobel A M, Wertheimer M R, Dib J and Schreiber H P 1980 *J. Macromol. Sci. Chem.* A **14** 321
[15] Poll H-U, Arzt M, Blaschta F, Friedrich M, Kreyßig E, Meichsner J and Rochotzki R 1993 Optische Eigenschaften von Plasmapolymerschichten *Final Report* (Germany: Technical University of Chemnitz)
[16] Sahli S, Segui Y, Hadj Moussa S and Djouadi A 1992 *Thin Solid Films* **217** 17–25
[17] Gazicki M, Wrobel A M and Kryszewski M 1984 *J. Appl. Polym. Sci. Symp.* **38** 1–19
[18] Mirabella F M 1998 *Modern Techniques in Applied Molecular Spectroscopy* (New York: Wiley)
[19] Pan Y V, Barrios E Z and Denton D D 1996 *Appl. Phys. Lett.* **68** (N24) 3386–8
[20] van Os M T, Menges B, Foerch R, Vancso G J and Knoll W 1999 *Chem. Mater.* **11** 3252–7
[21] Meichsner J and Li K 2001 *Appl. Phys.* A **72** (N5) 565–71
[22] Li K and Meichsner J 2001 *J. Phys.* D **34** (N9) 1318–25
[23] Yasuda H 1985 *Plasma Polymerization* (Orlando, FL: Academic)
[24] Hays A K 1982 *Proc. Electrochem. Soc. (Princeton, USA)* vol 82–86, pp 75–87
[25] Alexander M R, Jones F R and Short R D 1997 *J. Phys. Chem.* B **101** 3614–9
[26] Basner R, Foest R, Schmidt M, Becker K and Deutsch H 1998 *Int. J. Mass Spectrom.* **176** 245–52
[27] Chatham H, Hils D, Robertson R and Gallagher A 1984 *J. Chem. Phys.* **81** (N4) 1770–7
[28] Fan W Y, Knewstubb P F, Käning M, Mechold L, Röpcke J and Davies P B 1999 *J. Phys. Chem.* A **103** 4118–28
[29] 1974 *Eight Peak Index of Mass Spectra* vol I (London: Mass Spectrometry Data Centre, Elsevier) pp 1–2
[30] Scott D W, Messerly J F, Todd S S, Guthrie G B, Hossenlopp I A, Moore R T, Ann Osborn, Berg W T and McCullough J P 1961 *J. Phys. Chem.* **65** 1320–6
[31] Lin-Vien D, Colthup N B, Fateley W G and Grasselli J G 1991 *Handbook of IR and Raman Characteristic Frequencies of Organic Molecules* (London: Academic)
[32] Rau Ch and Kulisch W 1994 *Thin Solid Films* **249** 28–37
[33] Wright N and Hunter M J 1947 *J. Am. Chem. Soc.* **69** 803–9
[34] Socrates G 1994 *Infrared Characteristic Group Frequencies* 2nd edn (Chichester: Wiley) p 189
[35] Martinet C and Devine R A B 1995 *J. Appl. Phys.* **77** (N9) 4343–8