PLASMA POLYMERIZATION OF HEXAMETHYLDISILOXANE (HMDSO) IN RF CAPACITIVE DISCHARGE.

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Abstract

HMDSO deposition rate in dependence on the composite parameter ϕ introduced by Yasuda [1] is much the same by variation of discharge power as well as total gas pressure. Gas-phase plasma chemical conversion was studied by analysing the behaviour of the neutral components of HMDSO plasma. The fragmentation of monomer molecules in the plasma shows a stepwise character. Composition of the neutral component achieves a steady state after a characteristic time, which depends on discharge parameters. Plasma polymers have a monomer-like structure at low values of the parameter ϕ.

1. Introduction

Si-containing monomers, in particular HMDSO, are widely used in plasma assisted deposition processes (PECVD, plasma polymerization etc) in order to prepare thin films of technological interest: protective coatings [2], biomedical materials [3], permselective membranes [4], dielectric films [5], optical coatings [6]. In connection with that, the elementary processes, which take place in plasma and on a surface, as well as structure and properties of plasma polymer films have been intensively investigated.

Seefeldt et al. [7] investigated rigorously electron impact ionization of HMDSO. Plasma chemical gas conversion shows formation and consumtion of important stable compounds in a plasma reactor without gas flow [6]. This gas conversion is characterized by a stepwise formation of several groups of new compounds with time. The HMDSO content decreases continuously. Concentrations of oligomers as well as $Si(CH_3)_x$ groups grow in course of the time. These products are converted into low-molecular compounds (H_2, C_xH_y). High efficiency of the dissociation of HMDSO molecules into low-molecular fragments is confirmed by results of infrared absorption spectroscopy and optical emission spectroscopy [8].

By control of discharge parameters it is possible to vary the content of gas phase products and hence elementary composition and molecular structure of deposited films. Poll and co-authors [6] have shown that an increase of the total pressure reduces the content of SiO, SiH, OH, C=O bonds, whereas the concentration of CH, Si-CH_3 bonds grows. Kim [9] has studied the incorporation of Si-O-Si, Si-CH_3 groups in plasma polymer films by means of FTIR spectroscopy. He showed that concentrations of these specific Si-containing groups in plasma polymer films decrease with an increasing rf discharge power.

The aim of this work was to study the gas-phase conversion of HMDSO in rf discharge, the influence of discharge parameters on composition of the neutral component of HMDSO plasma as well as on the molecular structure of plasma polymers.

2. Experimental

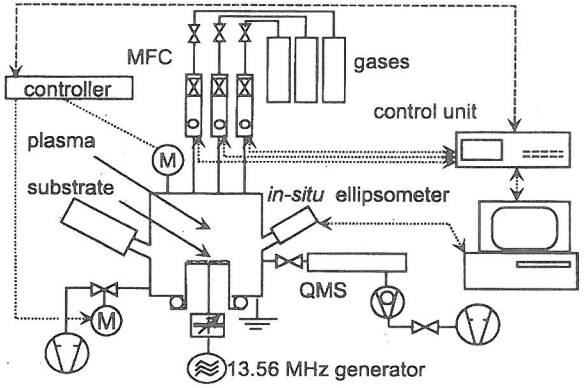

Figure 1. Schematic diagram of the experimental set-up

The experimental set-up is shown in Fig.1. Hexamethyldisiloxane or its mixture with high-purity Ar (99,999%) was supplied to the cylindrical vacuum chamber (20*l*) from the side feed line. The rf discharge was maintained by coupling an rf (13,56 MHz) generator to the substrate-carrying electrode against the grounded wall of the chamber through an automatic impedance matching network. The stable neutral products of gas conversion were investigated by mass spectrometry.

Film thickness and deposition rate were derived from *in-situ* ellipsometric measurements at a wavelength of 632,8 nm. Structure of deposited films was analysed by FTIR spectroscopy in the spectral range 3500 - 600 cm^{-1}.

3. Results and discussion

3.1. Macroscopic deposition kinetics

A complete microscopic describing of deposition kinetics is enormous difficult and in many cases unresolvable. The attempts, which have been made to describe the deposition of plasma polymer films, are based on the macroscopic kinetics, [1, 2, 9-14] one of the main tasks of which consists in understanding of the effect of the plasma process parameters on the basic plasma parameters as defined by Kay [15]. These are the electron density n_e, the electron energy distribution function $f(E_e)$, the gas density N and the residence time for a gas molecule in plasma τ. The possible approach to solve this task is the use of composite parameters. The meaning of most of them is the energy invested in plasma, which determines the efficiency of elementary (ionization etc) and chemical reactions [1, 10, 16]. We use the composite parameter ϕ, which describes the input energy per monomer molecule mass: $\phi = \frac{W \cdot kT}{p \cdot M \cdot f}$, where W is the discharge power, T is the gas temperature, p is the total gas pressure, M is the monomer molecule mass, f is the gas flow rate. Figure 2 shows the film deposition rate in dependence on this parameter. This behaviour can be understood with reference to the effect of process parameters on the basic plasma parameters. The raise of the parameter ϕ can be due to increasing discharge power or decreasing gas pressure at other fixed process parameters. Decrease of gas pressure leads to reduction of the gas density N and the residence time τ [17], but to an increase in electron density n_e and average electron energy $\langle E_e \rangle$ [18]. Enhancement of power leads also to an increase in average electron energy and electron density. In this way more electrons have energies above the characteristic threshold for dissociation, ionization etc. Variation of both process parameters results in the same dependency of the deposition rate on the parameter ϕ, see Fig.2. Increase

in average electron energy, electron density and density of energetic electrons leads to raise of the concentration of the active species, which take part in the film formation.

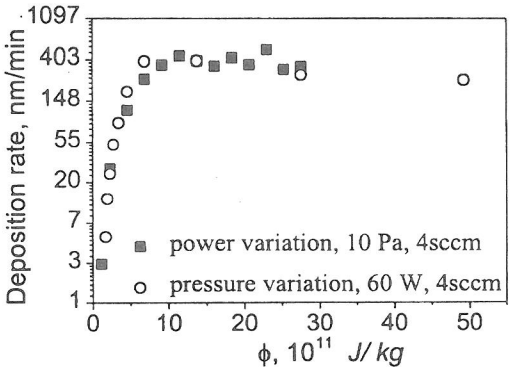

Figure 2. Dependency of HMDSO deposition rate on the composite parameter ϕ.

At high values of the parameter ϕ the deposition rate reaches a maximum level and depends slightly on the parameter. In this case monomer molecules are dissociated mainly into low molecular products such as hydrogen (H, H_2), C_xH_y molecules, which do not take part in the film formation. Moreover etching processes are in concurrence with deposition.

3.2. Mass-spectrometry of HMDSO monomer

Table 1. HMDSO mass-spectrum and appearance potentials (AP) of some neutral species.

m/z	rel. Intensity	species	AP, eV	Ref. [7]	Ref. [19]
162		$(CH_3)_6Si_2O$	8,9 ± 1,4	9,6 ± 1,0	8,8 ± 1,3
149	8,5	$(CH_3)_6\,{}^{28}Si\,{}^{29}Si\,O$	10,4 ± 0,6		9,6 ± 0,5
148	16,4	$(CH_3)_5Si_2OH$	10,4 ± 0,5		9,6 ± 0,5
147	100	$(CH_3)_5Si_2O$	7,7 ± 0,9;10,7 ± 0,7	10,4 ± 0,2	9,6 ± 0,5
133	0,8	$(CH_3)_4Si_2OH$	16,1 ± 0,6	17,7 ± 0,5	14,8 ± 0,9
131	3,8	$(CH_3)_3Si_2OCH_2$	15,1 ± 0,5	18,0 ± 1,0	15,8 ± 0,7
75	2,2	$(CH_3)_2SiOH$	14,1 ± 0,8		
74	2,1	$(CH_3)_3SiH$; $(CH_3)_2SiO$	14,2 ± 0,5		
73	24,8	$(CH_3)_3Si$	16,1 ± 1,1	18,7 ± 0,5	16,3 ± 0,6
66		$(CH_3)_4Si_2O$	26,1 ± 0,3	30,6 ± 1,0	26,8 ± 0,6
59	2,0	$(CH_3)_2SiH$; $(CH_3)SiO$	12,1 ±0,3; 22,2 ± 0,6	23,4 ± 1,5	22,0 ± 0,6
57	3,0	CH_3CH_2Si	11,8 ± 0,7		
56	3,1	CH_3CHSi	11,2 ± 0,5		
45	1,3	$(CH_3)SiH_2$; SiOH	21,3 ± 0,7	22,9 ± 1,6	25,3 ± 1,5
43	3,1	CH_3Si	14,3 ± 0,8;29,3 ± 1,1	30,0 ± 1,5	28,4 ± 0,7
15	3,2	CH_3	9,3 ± 1,0		14,7 ± 0,8
14	0,7	CH_2	13,5 ± 1,0		
2	14,6	H_2			

Mass spectrum of the pure monomer was studied at the plasma experiment conditions: gas pressure 10 Pa, gas flow rate 4 sccm, see Table 1. One should notice a dominant peak at 147 amu and a relatively high signal at 73 amu. Contrary to the literature data we did not detect a stable signal at 66 amu. Presented data correlate well with those already published in [7,19] and complement them partially. Seefeldt et al. [7] proposed a scheme of the formation of the neutral species with 147, 133, 131, 73, 59 amu. According their model, ionization of HMDSO molecules goes through O-atom as heteroatom, which

has free *p*-orbital electrons. Dissociation sequence looks like the following: monomer → fragment with 147 amu → fragments 133, 131, 74, 73, 59 amu.

3.3. Analysis of the neutral components of HMDSO plasma.

The stepwise character of the monomer molecule fragmentation can be more clearly observed in the plasma reactor without gas flow, see Figure 3.

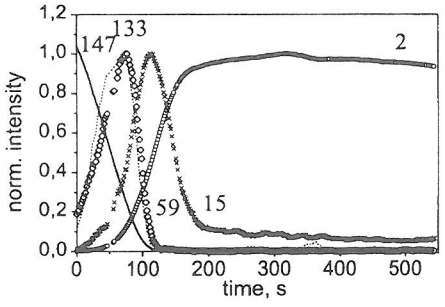

Figure 3. Plasma chemical conversion of HMDSO. Closed reactor, p_0 = 10 Pa, 60 W. Species (amu):
— (147); - - (133); ◊ (59); x (15); ○ (2)

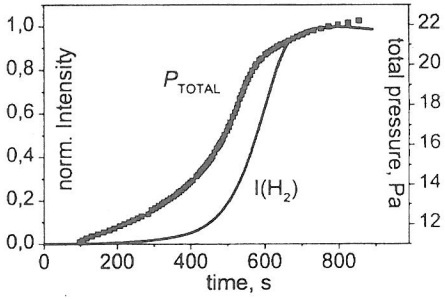

Figure 4. Time dependencies of the total pressure and the content of H_2. Closed reactor, 10 W, p_0 = 10 Pa.

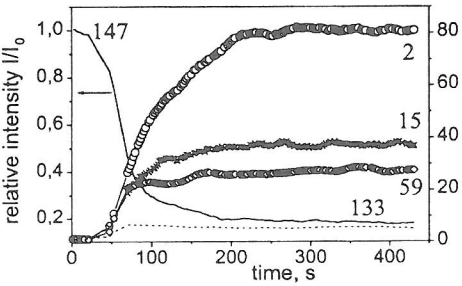

Figure 5. Gas-phase kinetics of plasma chemical transformation of HMDSO (M = 147 curve attributes to the left y-axis).
Discharge conditions:
10 Pa, 60 W, f_{total} 4 sccm, HMDSO:Ar 9:1

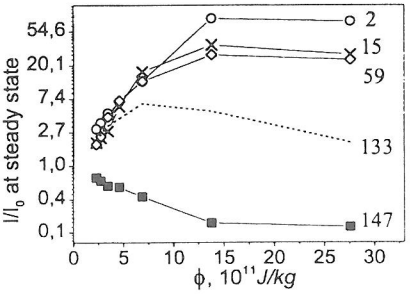

Figure 6. Dependencies of relative intensity at the steady state on the parameter ϕ.
Discharge conditions:
60 W, f_{total} 4 sccm, HMDSO:Ar 9:1

All detected neutral fragments can be classified into several groups according the behaviour of their kinetic curves: 'monomer' group - species with 162,149,147 amu; intermediate group - products of the 'first' step of dissociation with 133,131,75,74,73,59,45 amu; final products of full conversion - low-molecular weight species with 43,15,14 amu, atomic and molecular hydrogen (1, 2 amu). We show only several fragments to illustrate the overall dissociation character. The growth of pressure in the reactor is caused mainly by the increase

of low-molecular species, in particular molecular hydrogen. Qualitatively this suggestion is confirmed by comparison of the total pressure and the hydrogen content in dependence on time, see Figure 4. In the case of plasma with gas flow we observed the analogous trends except for the full conversion of the monomer molecules into the low-molecular products, see Figure 5. Composition of the neutral gas component achieves a steady state after a characteristic time, which depends on discharge parameters, see Figure 6. The content of the low-molecular species in the steady state is an increasing function of the composite parameter. The concentration of the fragments from 'monomer' group, species with 147 amu here, grows approximately linear with the pressure. The characteristic dissociation time of the fragment with 147 amu drops exponentially with the increase of the parameter ϕ.

3.4. Structure analysis of plasma polymer films

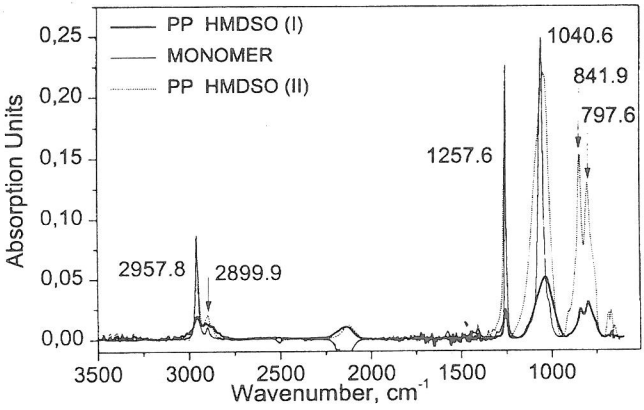

Figure 7.

Comparison of IR spectra of the monomer and plasma polymers.

Deposition conditions:

PP HMDSO (I) – 60 W, 10 Pa, 2 sccm;

PP HMDSO (II) – 10 W, 10 Pa, 8 sccm.

Mass-spectrometric data (Table 1) allow to propose that plasma polymers have more monomer-like structure at low values of the parameter ϕ, when the fragmentation of monomer molecules is weak.

Table 2. IR spectrum of HMDSO and PP HMDSO.

monomer	PP HMDSO(II)	Bond	Oscillation	Structure
Wavenumber, cm^{-1}				
2958,7	2957,8	C- H	asymmetric stretching	- CH_3
2900,9	2899,9	C- H	symmetric stretching	-CH_3
	2124,6	Si- H	stretching	Me_3Si-H
1413,3	1409,9	C- H	asymmetric deformation	Si-CH_3
1252,7	1257,6	C- H	symmetric deformation	Si-CH_3
1054,1	1040,6	Si- O	asymmetric stretching	Si-O-Si
	841,9	Si- O	symmetric stretching	Si-OH
	797,6	CH_3	rocking	Si-CH_3
	685,7	Si- C	symmetric stretching	Si-$(CH_3)_3$
	671,2	Si- C	symmetric stretching	Me-Si-Me
	651,9	Si- C	asymmetric stretching	Si-$(CH_3)_3$

In the other case it should be expected lower concentrations of siloxane bonds or Si-C bonds in films, deposited at high values of the composite parameter. Therefore plasma polymer films of about 1 μm thickness were deposited on Si-wafers in experiments of two essentially different kinds. A summary of the characteristic oscillations of some bonds is presented in the Table 2. The infrared spectra of the monomer as well as plasma polymer films confirm the supposition, see Figure 7.

4. Conclusions

Variation of discharge power as well as gas pressure leads to the same dependency of HMDSO deposition rate on the composite parameter ϕ. Gas-phase plasma chemical conversion shows the stepwise character. The grade of dissociation depends on the parameter ϕ. High-molecular products of the dissociation dominate in the gas-phase at low values of the parameter ϕ, which determines the monomer-like structure of plasma polymers deposited at the appropriate process conditions. The content of Si-containing groups in plasma polymer films drops drastically at high values of the composite parameter.

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