

PLASMA POLYMERIZED HEXAMETHYLDISILOXANE THIN FILMS FOR NO₂ GAS SENSOR APPLICATION

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Plasma polymers are synthesized from hexamethyldisiloxane by capacitively coupled glow discharge. The effect of current density and monomer flow rate on the polymer structure is investigated by FTIR spectroscopy. The influence of the same parameters on the NO₂ sensing properties of the polymers is studied by a quartz crystal microbalance.

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1. Introduction

In the recent past, plasma polymerization has been employed as an attractive method for obtaining thin films. Because of the mechanism of the plasma process the structure of the plasma polymers substantially differs from the conventional polymers. The highly branched and cross-linked network determines a set of useful properties: mechanical toughness, thermal stability, chemical resistance etc.[1-3]. That is why originally they were widely used as protective coatings [4]. More over the chemical structure of the plasma polymers depends not only on the used monomer, but on the plasma polymerization conditions as well. By varying different parameters, films with desired chemical structure and properties could be obtained. Therefore there is a possibility to expand this technology to other applications. Recently, there is an interest of using plasma polymers as sensitive films in chemical sensors [5-9]. The organosilicon plasma polymers are of particular interest for sensor applications. For example, polymers obtained from hexamethyldisiloxane (HMDSO) are very widely used in sensors [10-16].

The paper presents results on the effect of glow discharge current density and monomer flow rate on the chemical structure of plasma polymers obtained from HMDSO. The sensing properties to NO₂ of polymers obtained are studied as well. The polymer structure is studied by FTIR spectroscopy. Polymer mass changes resulting from NO₂ sorption are registered by a quartz crystal microbalance (QCM). The influence of the ammonia plasma modification on the NO₂ sensing properties of the polymers is investigated.

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2. Experimental

2.1 Synthesis of plasma polymerized HMDSO films (PPHMDSO)

The plasma polymerization process was performed in a vacuum system described in details previously [17]. In the reactor chamber the capacitively coupled glow discharge was accomplished between two horizontally aligned aluminum electrodes positioned at a distance of 60 mm. The monomer hexamethyldisiloxane (HMDSO) was purchased from Merck, Germany >99%. The plasma excitation of the HMDSO gas was achieved at 27.12 MHz using a generator (VEM Inducal Berlin, Germany). The dosage of the monomer and ammonia vapors was carried out by a regulator for gas consumption (GMR, NOVIS, Bulgaria). The substrates, quartz resonators (for studying sorptive properties of the layers) and KBr pellets (for studying the FTIR spectra) were located on a Teflon plate placed between the electrodes at a distance of 30 mm from each of them. The deposition on the two kinds of substrates was performed simultaneously under the same conditions for 20 minutes. The plasma polymerization was controlled by two parameters: the current density of the glow discharge and the monomer flow rate. The current density was 0.16 mA cm⁻² and 0.32 mA cm⁻² and the monomer flow rate varied from 0.004 sccm to 0.024 sccm. The polymer film thickness estimated from the frequency shift of the QCM before and after polymer deposition (according to the Sauerbrey equation [18]) was of about 200 nm. The modification of the films with ammonia plasma was carried out at constant conditions: 0.024 sccm NH₃ flow rate and 0.16 mA cm⁻² current density for 7 minutes. The treatment with ammonia was aimed at increasing the gas sorption of the PPHMDSO films.

2.2 Material characterization

FTIR absorbance spectra of the PPHMDSO films were recorded by a spectrophotometer Bruker Tensor 27 in the 4000-600 cm⁻¹ spectral region with a resolution of 2 cm⁻¹.

A laboratory setup used for studying the sensitivity to NO₂ of PPHMDSO thin films deposited on quartz resonator used as QCM was described in [19]. Dry synthetic air and 1 % NO₂ gas were used. The NO₂ concentrations in the test camera were created by changing the ratio of the NO₂ gas and the diluting gas flow. The working temperature was 26 ± 0.2°C. The coated QCM frequency was registered continuously by a counter connected to the QCM and to a computer. The process of measurement can be divided into three stages: purging the polymer – QCM system by dry air until the frequency reaches a constant value; creating a certain NO₂ concentration and reaching saturation of the frequency value and purging the camera with dry air thus restoring the sample. The NO₂ concentrations ranged from 100 ppm to 5000 ppm.

3. Results and discussion

3.1 FTIR study

The plasma polymers (PPs) predominantly form irregular and amorphous structure that obstructs its exact determination. Moreover, it is known that the structure of PPs, albeit one and the same monomer is used, is genetically altered, depending on the operating conditions. To study the influence of the main plasma parameters, namely, the monomer flow rate and the glow discharge current density on the PPs structure, infrared spectroscopy was employed.

It is known that vibrational bands in the IR spectra of plasma polymers are very sensitive to a changed neighboring environment in the polymer structure. Table 1 contains the principal vibrational band frequencies and their tentative assignments, on the base of previous studies of plasma polymers, obtained from HMDSO [20-22].

Table 1. IR absorption bands of PPHMDSO and their assignment (e.g.Refs.[20-22])

Wave number [cm^{-1}]	Assignment
775	$\rho(\text{CH}_3)$ in $\text{Si}(\text{CH}_3)_n$, $n=1,2$
837	$\rho(\text{CH}_3)$ in $\text{Si}(\text{CH}_3)_n$, $n=2,3$
1036	$\nu_s\text{Si-O-Si}$
1066	$\nu_a\text{Si-O-Si}$
1265	$\nu_s\text{Si}(\text{CH}_3)_n$, $n=1,2$
1452	$\delta_a(\text{CH}_2)$ in $\text{Si-CH}_2\text{-Si}$
1600-1630	$\delta_s(\text{OH})$
2853	$\nu_s(\text{CH}_2)$ in Si-CH_2
2872	$\nu_a(\text{CH}_2)$ in Si-CH_2
2924	$\nu_s(\text{CH}_2)$
2965	$\nu_a(\text{CH}_3)$
3183	$\nu(\text{OH})$

The FTIR spectra of the PPs obtained at diminishing monomer flow rate keeping the current density constant (0.32 mA cm^{-2}) are displayed on Figure 1(a,b,c).

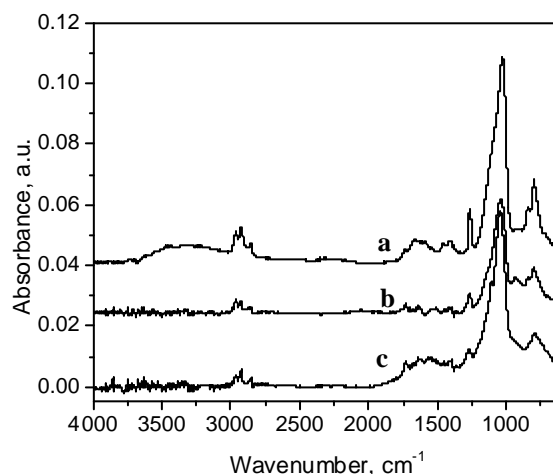


Fig.1 FTIR spectra of PPHMDSO obtained at current density of 0.32 mA cm^{-2} and monomer flow rate of: a – 0.024 sccm ; b – 0.011 sccm ; c – 0.004 sccm .

The most intense band due to the Si-O stretching vibrations at about 1030 cm^{-1} showed weak wavenumber up-shift with decrease of the monomer flow rate level. The reduction of the monomer flow rate also leads to more pronounced intensity increase of the Si-CH₃ stretching absorption at 799 cm^{-1} , originating from Si-(CH₃)₂ and Si-CH₃ groups, in comparison to 846 cm^{-1} absorption [Si-CH₃ stretching in Si-(CH₃)₃ end groups]. This certifies that more CH₃ groups have been removed from monomer molecule during the polymerization process at smaller flow

rate. Another support for this supposition is the amplitude behavior of the Si-(CH₃)_{2,1} symmetric stretching band at 1268 cm⁻¹. The reduction of the monomer flow rate at a constant current density results in augmentation of the plasma power per unit monomer molecule. This in turn causes additional abstraction of hydrogen atoms and methyl groups. The diminishing number CH₃ groups per atom Si at reduced monomer flow rate could be an indication of a long-chain polymer containing more Si-O cross-links. The increase of the CH₂ stretching band intensities at 2852 cm⁻¹ and 2924 cm⁻¹ (symmetric and antisymmetric vibrations, Fig 1a) suggests that at higher monomer flow rate more Si-CH₂-Si fragments are being created. According to our previous study on the structure of the same polymer and additional literature it could be considered that these peaks are characterizing CH₂ groups in Si neighboring environment [17, 22]. The enhanced amplitude of the band at 1459 cm⁻¹, which was found to originate from CH₂ scissoring vibration of Si-CH₂-Si fragments, confirmed this assumption. The results suggested that the decrease of the monomer flow rate leads to elongated and more branched polysiloxane chain where the number of Si-CH₂-Si fragments decrease at the expense of predominantly Si-O-Si bridges.

The effect of the glow discharge current density on the FTIR spectra of the PPHMDSO films is presented in Figure 2. The current density increase caused an intensity raising and broadening of the Si-O absorption from 1030 to 1200 cm⁻¹. It is obvious that the most intensive band in the spectra contains more than one peak hidden under the broadband contour. It originates from Si-O vibrations, which could experience different environments in the polymer network.

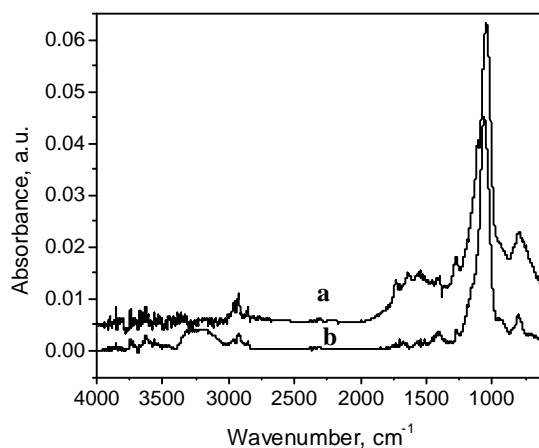


Fig.2. FTIR spectra of PPHMDSO obtained at monomer flow rate of 0.024 sccm and current density of: a - 0.32 mA cm⁻²; b - 0.16 mA cm⁻².

Two bands located at 1044 and 1108 cm⁻¹ could be found [20]. The first band originates from Si-O vibrations in Si-O-Si groups [20, 21], whereas the second is likely related to Si-O vibrations in a changed neighboring environment where also Si-CH₂-Si groups are involved. The enhanced intensity and broadening of the peak at higher current density pointed to an elongation of the main chain as well as to a high degree of cross-linking mainly due to oxygen atoms in Si-O-Si groups. As a result the oxygen content in the polymer increased. The oxygen atoms could be adsorptive centers for NO₂ molecules on the base of intermolecular forces.

The ammonia plasma modification aims to create suitable centers for improving gas sorptions by the polymer surface. At first glance the FTIR spectra of treated and untreated PPHMDSO films do not differ significantly (Fig. 3).

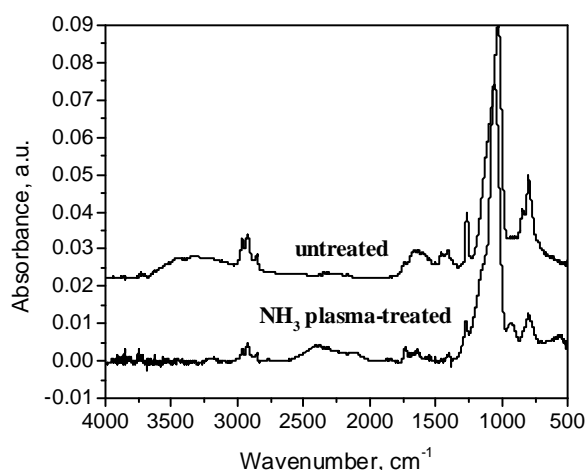


Fig.3. FTIR spectra of NH_3 modified and unmodified PPHMDSO obtained at monomer flow rate of 0.024 sccm and current density of 0.32 mA cm^{-2} .

Closer inspection of the NH_3 modified polymer spectrum, however, revealed noticeable decrease of the amplitude of some bands for the C-H stretching vibrations located at 2960 cm^{-1} and 2918 cm^{-1} , and also the bands of 837 cm^{-1} and 800 cm^{-1} , caused by methyl rocking vibration in a $\text{Si}(\text{CH}_3)_3$ groups and in $\text{Si}(\text{CH}_3)\text{Si}(\text{CH}_3)_2$ groups, respectively. The decrease of the amplitude of the bands concerning CH_x groups is a clear indication that the ammonia plasma cleaved additional hydrocarbon fragments from the polymer surface. It could be difficult to claim whether some NH_x groups are attached to Si or C atoms, because both the corresponding Si-N and C-N band would be hidden under the broadband contour of the Si-O bands. The frequency shift to higher wavenumber and the higher intensity of the Si-O band showed that Si-O-Si groups are predominantly embedded in the polymer surface network after ammonia treatment. As a result additional Si-O-Si bridges have been created which seem to prevail over the Si-N bond formations. Presumably, the NH_3 plasma treated films have higher degree of cross-linking due to the decrease of hydrocarbon groups and therefore an increase of Si-O-Si fragments on the polymer surface. The final effect is oxygen content increase, which could provide an increase of the intermolecular forces between the polymer film and NO_2 gas molecules.

3.2. Gas sensing properties to NO_2 of the PPHMDSO films

In our previous investigations with PPHMDSO as active layer in different piezoelectric sensors was established its stable behavior after more than 2 cycles [13,14]. Having in mind this results in the present experiments the purpose was to follow the kinetics of the process of sorption. The gas sensing properties of the polymer films were estimated by measuring the frequency-time characteristics (FTC) of the polymer coated QCM at NO_2 concentrations ranging from 100 ppm to 5000 ppm. A typical example of a FTC of a polymer-QCM structure to certain NO_2 concentration is presented in Figure 4.

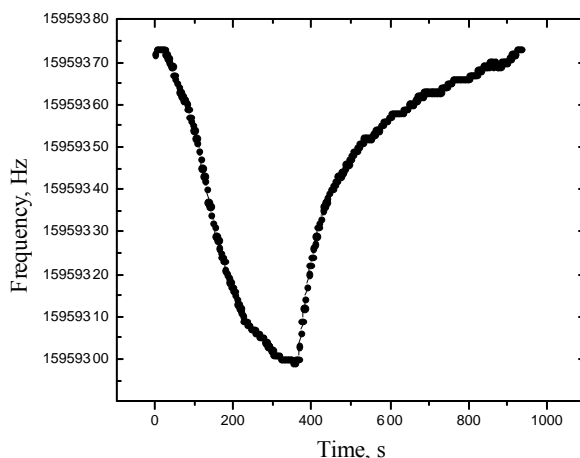


Fig. 4. FTC of a polymer – QCM structure at 100 ppm NO_2 concentration.

The regeneration of the samples for all concentrations shows that the process of NO_2 sorption is reversible and has a physical nature. The frequency response of a polymer-QCM system to NO_2 concentration is demonstrated in Figure 5.

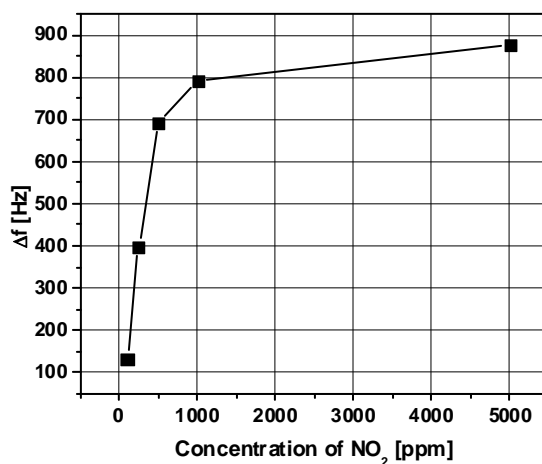


Fig.5. Frequency shift of a polymer-QCM structure vs NO_2 concentration.

The dependence is non-linear. It is seen that the sensitivity to NO_2 is much higher up to 1000 ppm. At concentrations higher than 5000 ppm the frequency change is negligible higher than those for 5000 ppm. Probably the saturation of the film was observed.

The effect of the investigated plasma parameters and ammonia plasma treatment on the NO_2 sensing properties of the polymer films is shown in Table 2.

Table 2. Frequency shift of the polymer-QCM structures at different NO₂ concentrations, depending on plasma parameters and ammonia modification.

Monomer flow rate [sccm]	Current density [mA cm ⁻²]	NH ₃ modification	Frequency shift [Hz]				
			NO ₂ concentration [ppm]				
			100	250	500	1000	5000
0.024	0.16	–	–	23	40	57	72
0.024	0.16	+	24	40	62	89	114
0.024	0.32	–	5	30	60	97	135
0.011	0.32	–	79	160	241	287	326
0.004	0.16	–	78	156	238	286	318
0.004	0.32	–	106	212	267	323	399
0.004	0.32	+	140	397	691	790	878

The decrease of the monomer flow rate and the increase of the current density led to increased sorption of the NO₂ molecules. Presumably the higher oxygen content was the reason for improved sorption ability toward studied NO₂ gas molecules. Probably the oxygen atoms were adsorptive centers for NO₂ gas molecules due to intermolecular forces. That is why the process of sorption is reversible and therefore has physical nature.

It is evident from Table 2 that the sensitivity to NO₂ films, treated with ammonia, is higher than for films without treatment at the same deposition conditions. The results showed that due to ammonia plasma modification the structural changes in the polymer surface (mainly higher oxygen content) lead to an increase of NO₂ sorption.

4. Conclusion

The study on the PPHMDSO thin films synthesized at different plasma conditions were presented in order to use them as a sensitive layer in acoustoelectronic sensors.

The FTIR spectroscopic study revealed that the investigated plasma parameters significantly influence the chemical structure of the polymers. The result of the current density increase and the accompanying monomer flow rate decrease has an effect of elongated and additionally cross-linked polysiloxane chain. The ammonia plasma post treatment led to creation of additional Si-O-Si bridges in the polymer network. The higher oxygen content contributed to the enhanced sorptive characteristics of the plasma polymer films with respect to the studied gas molecules. It is probably due to the creating intermolecular forces between oxygen atoms and NO₂ molecules, which results in a better performance of the sensor's element.

The increase of the glow discharge current density and the decrease of the monomer flow rate led to augmented NO₂ gas sorption detected by polymer-QCM system. The modification by ammonia plasma increases the NO₂ gas sorption of plasma polymers. This study proved that thin-layer QCM systems suitable for NO₂ detection could be developed in the concentration interval within the limits from 100 ppm to 5000 ppm.

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