

Fourier Transform Infrared Analysis of Hexamethyldisiloxane Layers Obtained in Low-Frequency Glow Discharge

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SYNOPSIS

Polymer layers from hexamethyldisiloxane (HMDSO) up to 1 μm were produced by glow discharge at 50 Hz under different polymerization conditions. The Fourier transform infrared (FTIR) spectra of such layers were obtained at different current densities of the glow discharge (0.53 to 3.10 mA/cm^2), substrate temperatures from 35 to 125°C; gaseous phase pressures from 13.3 to 266 Pa, and layer thicknesses from 0.2 to 0.6 μm . The FTIR spectra of polyhexamethyldisiloxane (PHMDSO) layers modified after treatment in ammoniacal plasma were studied. The spectra of layers obtained in plasma containing both monomer and ammonia vapors were also analyzed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Plasma polymerization is used to produce polymer layers of organic compounds that do not polymerize under normal (chemical) polymerization conditions. Plasma polymerization is a process of thin-film formation in which the monomer, subjected to successive fragmentation and recombination, forms a polymer.¹ Inagaki et al.² suggested that the chemical structure of the plasma polymer strongly depends on the fragmentation process of the polymer in the plasma. This fragmentation process depends not only on the chemical composition and structure of the monomer but on the parameters of the polymer deposition process in the glow discharge as well.³ By varying different parameters, materials with different chemical compositions and different structures could be obtained. These materials could be deposited on the substrate in the form of powder, thin films, or their combination. Such polymers usually have highly branched and cross-linked chemical structure. They hardly dissolve or do not dissolve at all in acids, alkali, and some organic solvents.^{4,5} Of great interest are polymer layers, plasma-depos-

ited onto the surface of a quartz resonator, which could be used as a highly sorptive sensor for measuring the relative humidity of the air. For this purpose, it is necessary to avoid the negative effects of some gases upon the quartz resonator surfaces, as well as to ensure a selective sorption of water molecules from atmospheric air. Technological conditions for preparing such sensors and their physical properties are described in Refs. 6–10. The aim of the present work was to analyze Fourier transform infrared (FTIR) spectra of thin polyhexamethyldisiloxane (PHMDSO) layers obtained in glow discharge at a frequency of 50 Hz. The following parameters were varied: glow discharge current density, gas medium pressure, temperature of the substrate, and layer thickness. Also studied were the FTIR spectra of layers formed in plasma containing both HMDSO monomer and ammoniacal vapors, as well as spectra of PHMDSO layers obtained after modification of HMDSO in ammonia plasma.

EXPERIMENTAL

The reactor for polymer layer deposition was connected to a vacuum installation. The aluminum glow discharge electrodes (80 cm^2) were placed horizontally 20 mm above each other. The polymer layers were deposited on KBr pellets (for studying the

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FTIR spectra) and on the surface of the quartz resonator with gold electrodes (for studying the physical parameters of the layer at the macrolevel). KBr pellets were placed on the lower electrode or about 5 mm above it. The quartz resonators were placed about 5 mm above the lower electrode.

The lower electrode temperature and the temperature of KBr pellets placed above it were measured by a platinum thermosensor. The layer thickness was determined by the quartz resonator frequency change (Δf). The polymer deposition on the resonators and on the KBr pellets was performed simultaneously under the same conditions. The pressure of the gas medium was measured with a WN221 Vakuummeter (VEB HOCHVAKUUM, Dresden), calibrated for air. The dosage of the monomer and ammonia vapors was carried out by special inlet microvalves. The glow discharge voltage was about 400 V, 50 Hz; the current density varied from 0.5 to 3.0 mA/cm² depending on the experimental conditions. The polymer deposition duration varied from 6 to 15 min. The temperature of the KBr pellets above the lower electrode was 35°C at the 6th min and 65°C at the 15th min of polymerization at maximum current density. At lower current densities, the measured temperatures were lower.

The modification of the deposited PHMDSO layer with ammonia vapors was carried out in the

same reactor for about 7 min, at the same current density and pressure. The treatment with ammonia was aimed at increasing the humidity selective sorption of the PHMDSO layer, i.e., at transforming it from hydrophobic to hydrophilic. FTIR spectra of polymer layers were obtained using a Bruker IFS113v spectrophotometer.

RESULTS AND DISCUSSION

The spectra of HMDSO monomer and the corresponding plasma polymer are presented in Figure 1(a) and (b). The monomer showed characteristic methyl (CH₃) stretching bands at 2958 and 2899 cm⁻¹ (asymmetric and symmetric vibrations). The corresponding bending bands appeared at 1441 and 1412 cm⁻¹. Other characteristic bands were Si—CH₃ rocking at 1254 cm⁻¹ and (Si—CH₃)₃ stretching vibration at 847 cm⁻¹. The Si—O bond appeared as a strong band at 1053 cm⁻¹.

Plasma polymerization is considered as a process of fragmentation of the monomer in the plasma field and a successive recombination of the split radicals.^{1,5} Some data from chromatographic studies of pyrolysis products of polymerized organosiloxanes,⁶ as well as earlier studies of IR spectra,⁷⁻⁹ support the assumption that some methyl groups were removed from the monomer molecule during the po-

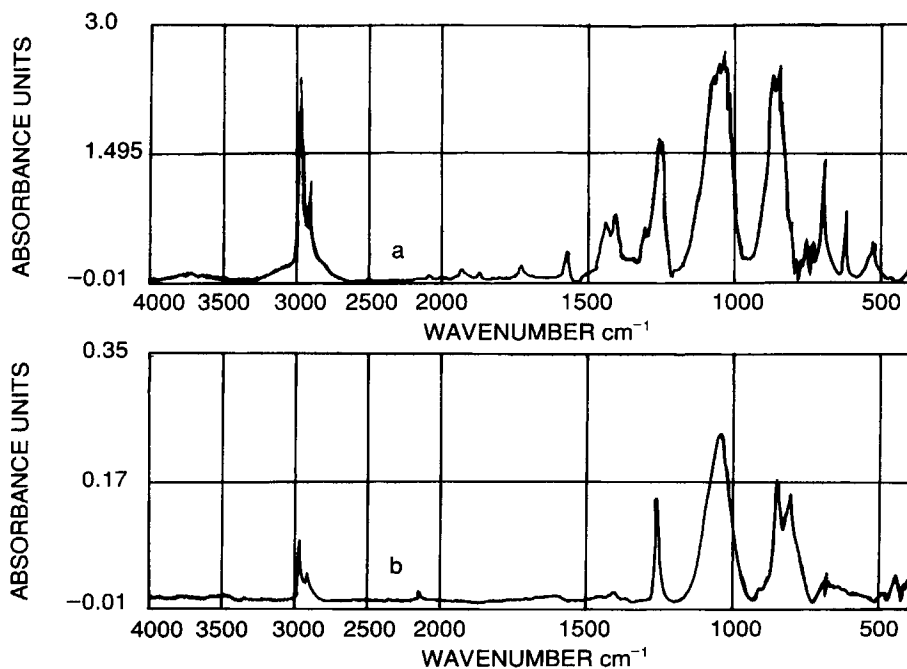


Figure 1 FTIR spectra of (a) monomer HMDSO dissolved in CCl₄, 0.2 mm KBr cell and (b) its plasma polymer, deposited on a KBr pellet.

lymerization process. Figure 1(b) confirms this assumption. The methyl band at 2958 cm^{-1} decreased in intensity; the corresponding methyl bending bands could hardly be distinguished. Considerably more intense were the bands connected with the vibrations when the Si atoms take part. It could be concluded that during polymerization the number of CH_3 groups per atom Si decreased as compared to the monomer.

Polymerization resulted in considerable increasing of intensity and widening of the Si—O stretching band. This could be an indication of a long-chain polysiloxane¹⁰ and/or of the contribution from the CH_2 group from Si— CH_2 —Si bonds, formed after hydrogen abstraction.⁸ The removal of some CH_3 groups during polymerization resulted in the ap-

pearance of a second Si— CH_3 band at 798 cm^{-1} that was absent in the monomer spectrum and that indicated the existence of Si— $(\text{CH}_3)_2$ and Si— CH_3 end groups.⁹ Other characteristic bands were Si— $(\text{CH}_3)_3$ stretching at 840 cm^{-1} , with decreased intensity as compared to its analog in the monomer spectrum, and Si— CH_3 rocking vibration, its diminishing being an indication of a branched polymer.¹¹

The effects of plasma parameters on the FTIR spectra of plasma-polymerized HMDSO have been studied by several authors.^{8,9,11} Usually, the monomer behavior is studied at different current densities, the pressure of the monomer gas in the reactor being held constant. This leads to an increase of the energy per unit mass of the monomer, thus changing its

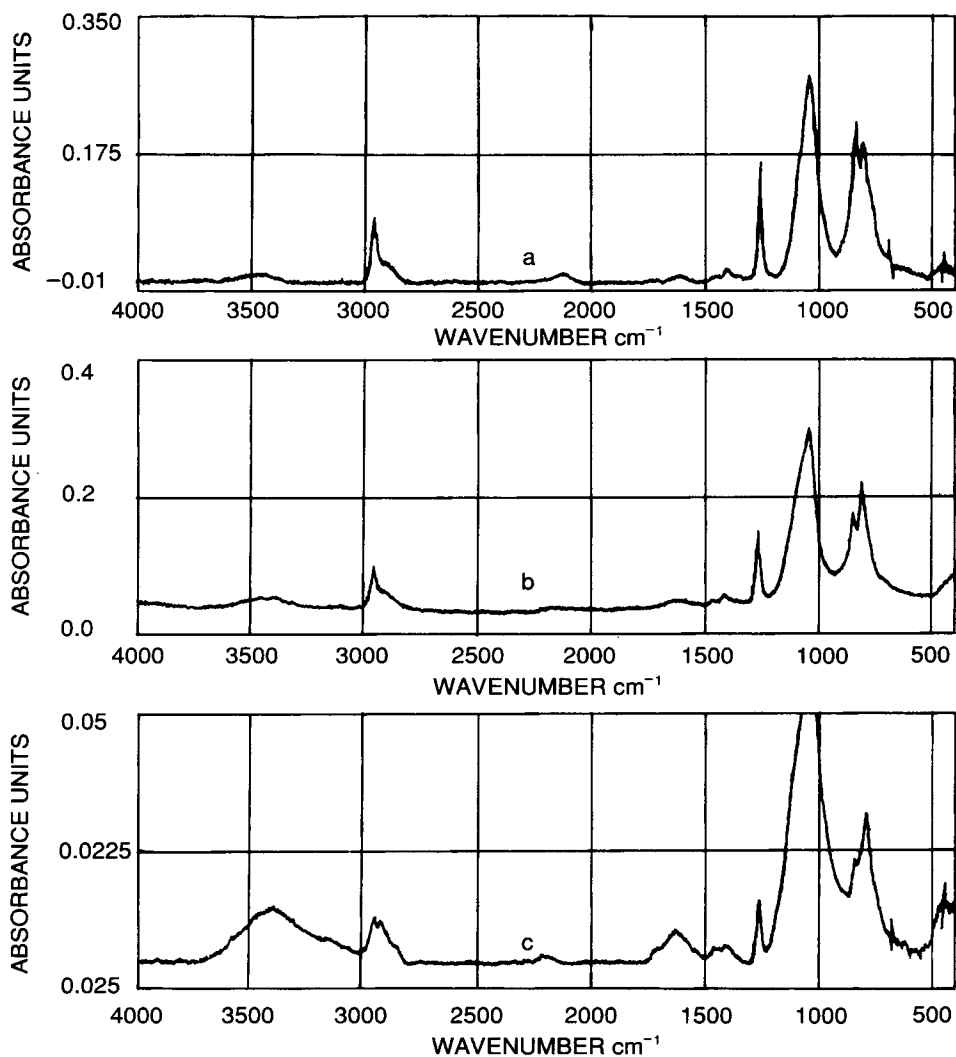
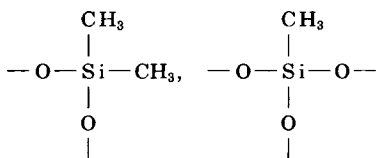


Figure 2 FTIR spectra of plasma polymerized HMDSO at different discharge current densities: (a) 0.53 mA/cm^2 ; (b) 1.10 mA/cm^2 ; (c) 1.43 mA/cm^2 .

fragmentation in the plasma field. It has been argued by Assink et al.¹² and Tajima and Yamamoto¹³ and confirmed by Krishnamurthy et al.¹⁴ that an enhancement of the plasma power results in an increased number of the following units in the polymer chain:



Evidence supporting these conclusions can be found in our investigations of the FTIR spectra of HMDSO plasma polymer obtained at different discharge current densities and at 50 Hz frequency [Fig. 2(a)–(c)]. Our data were obtained at low frequency (50 Hz), whereas other authors worked at high frequencies. The increase of plasma power led to a proportional increase of the Si—CH₃ absorption at 798 cm⁻¹ due to Si—(CH₃)₂ and Si—CH₃ groups in comparison to 840 cm⁻¹ absorption [Si—CH₃ stretching in Si—(CH₃)₃ end groups]. This indicates that more CH₃ groups are removed during plasma treatment at higher current densities. The Si—O stretching absorption at 1043 cm⁻¹ showed

no systematic change with plasma level. Its higher intensity and broadening pointed to an elongation of the polymer chain,¹⁰ as well as to a high degree of cross-linking. For the current density range indicated in Figure 2, we did not observe a splitting of this band. A well-pronounced shoulder at the long wavenumber end of this band was observed at higher power levels. The weak absorption at 2100 cm⁻¹, well resolved at lower current densities, could be assigned to the Si—H stretching vibration.

The polymer thickness depended on the duration of treatment in plasma, other conditions being held equal. Thickness changes within the 0.25–0.55 μm range did not affect the type of FTIR spectra (Fig. 3). Polymer layers were obtained at 3.06 mA/cm² and 266 Pa. Figure 3(a) shows 0.25 μm thickness and 6 min duration of deposition; Figure 3(b) shows 0.55 μm thickness and 16 min duration of deposition. The absorption bands of both IR spectra were the same: 2958 and 2899 cm⁻¹ (asymmetric and symmetric vibrations), Si—CH₃ rocking at 1254 cm⁻¹, Si—(CH₃)₃ stretching vibration at 847 cm⁻¹, and an Si—O bond appearing as a strong band at 1053 cm⁻¹.

To measure the temperature effects on the structure of the polymer during glow discharge polymerization, KBr pellets were placed on the electrode

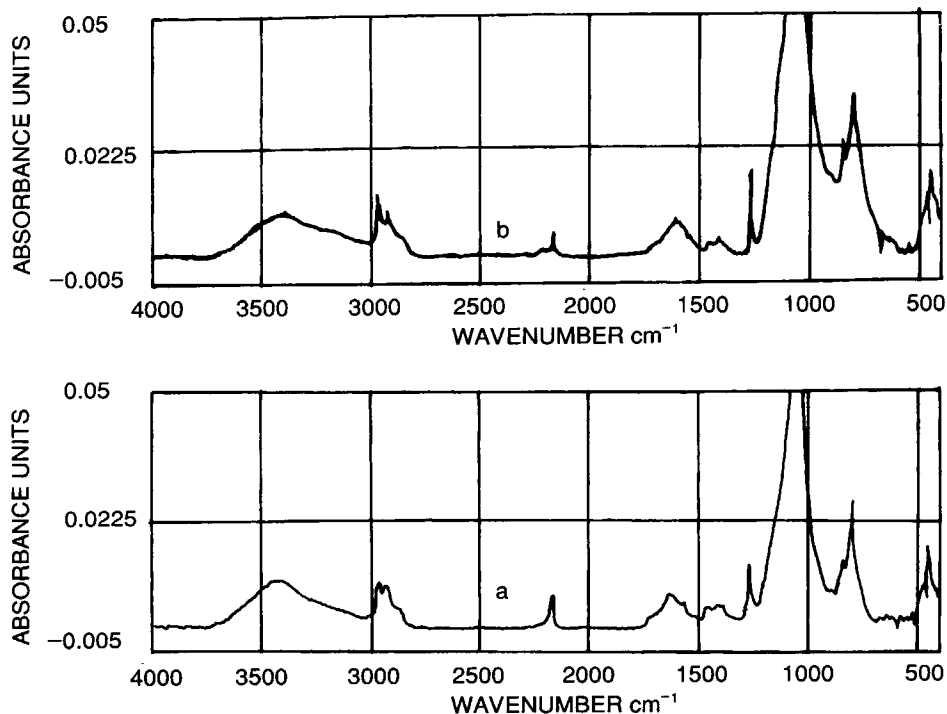


Figure 3 FTIR spectra of plasma-polymerized HMDSO with different thicknesses: (a) 0.25 μm; (b) 0.55 μm.

and 5 mm above the electrode. The temperature of the KBr pellets above the lower electrode was 35°C at the 6th min and 65°C at the 15th min of polymerization at maximum current density. During polymerization, the temperature of the lower electrode increased from 25 to 125°C. No changes were observed in the FTIR spectra (Fig. 4) of layers deposited on the pellets at different temperatures, i.e., the FTIR spectra were the same regardless of the temperature change of the substrate.

The FTIR spectra of the polymers, obtained at 266 and 106 Pa gas medium pressure during polymerization, are shown in Figure 5(a) and (b). There are absorption bands at 2958 and 2899 cm^{-1} (asymmetric and symmetric vibrations), Si—CH₃ rocking at 1259 cm^{-1} , Si—O bond vibration at 1030 cm^{-1} , Si—(CH₃)₃ stretching vibration at 841 cm^{-1} , and Si—CH₂ asymmetric vibrations at 796 cm^{-1} [Fig. 5(b)]. The spectrum in Figure 5(a) shows absorption bands only of the Si—O bond (1060 cm^{-1}) and of the Si—H bond (2100 cm^{-1}). Hence, the substances that we have obtained were of different chemical compositions and structures. The absorption bands at 2958 and 2899 cm^{-1} (asymmetric and symmetric vibrations), Si—CH₃ rocking at 1259 cm^{-1} , Si—(CH₃)₃ stretching vibration at 841 cm^{-1} ,

and Si—CH₂, which characterized the organic nature of the deposited layer, disappeared.

The FTIR spectra of the nonmodified HMDSO polymer, obtained at 1.1 mA/cm^2 current density, 133 Pa gas medium pressure, and 0.25 μm layer thickness are shown in Figure 6(a). After deposition, the polymer was treated with ammonia in plasma under the above conditions. The FTIR spectra of the polymer are shown in Figure 6(b). No other absorption bands in the FTIR spectra due to ammonia were observed. Polymer plasma layers with 0.9 μm thickness were obtained in a mixture of monomer and ammonia vapors at 2.55 mA/cm^2 current density and 266 Pa pressure. The FTIR spectra of these layers did not differ from the spectra in Figure 6(a), i.e., no new absorption bands were observed. This indicates that no compositional and structural changes of the polymer occurred.

CONCLUSIONS

The glow discharge current density at low frequency (50 Hz) strongly influenced the FTIR spectra of the HMDSO polymer. The increase of the current density increased the intensity of the bands at 800 cm^{-1}

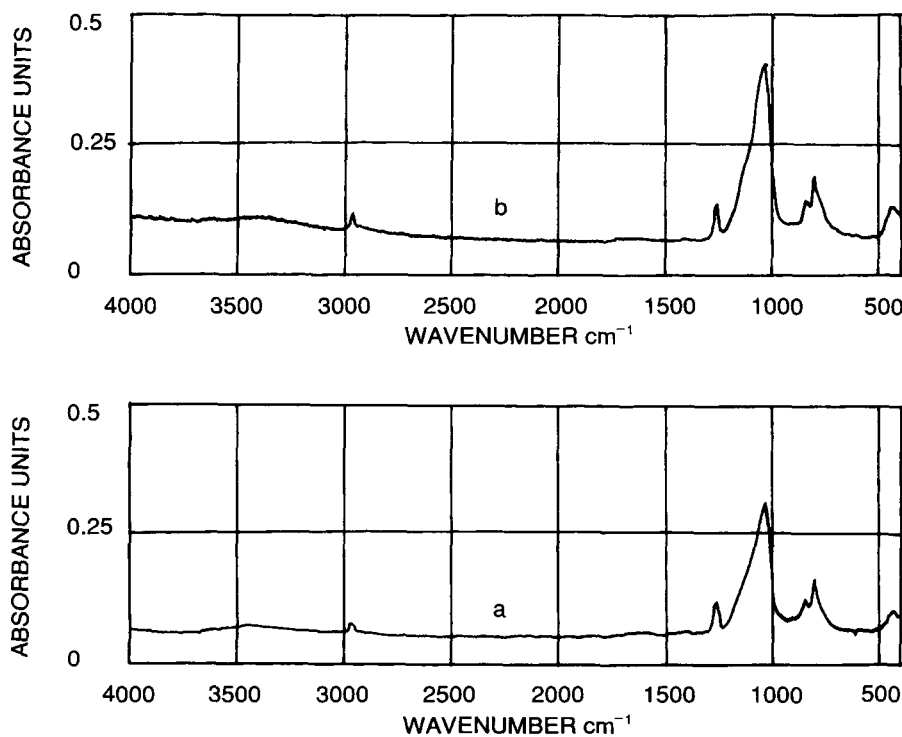


Figure 4 FTIR spectra of plasma polymerized HMDSO: (a) KBr pellet on the electrode; (b) KBr pellet on 5 mm above the electrode.

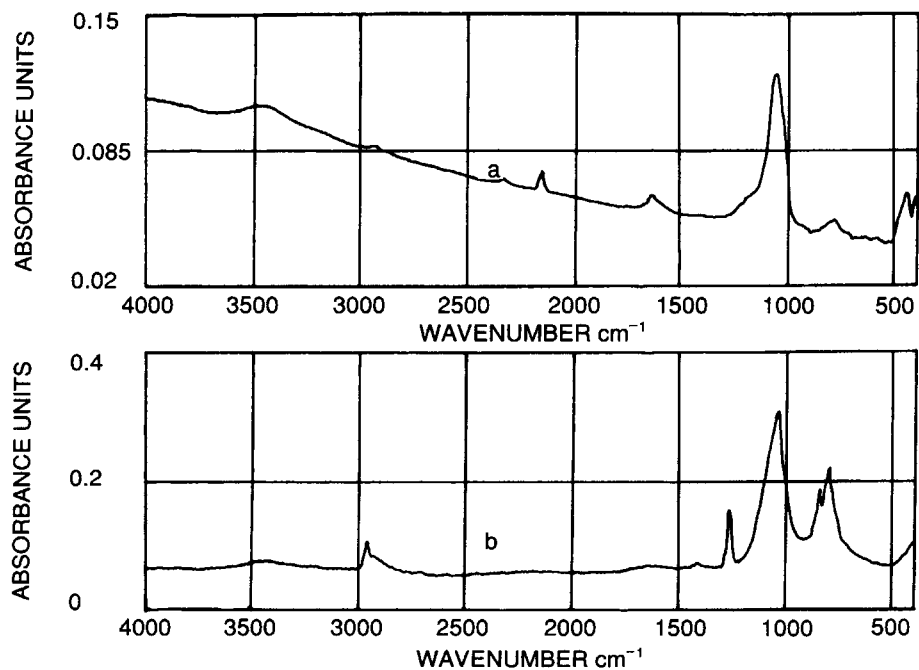


Figure 5 FTIR spectra of plasma polymerized HMDSO obtained at different gas-phase pressures: (a) 266 Pa; (b) 106 Pa.

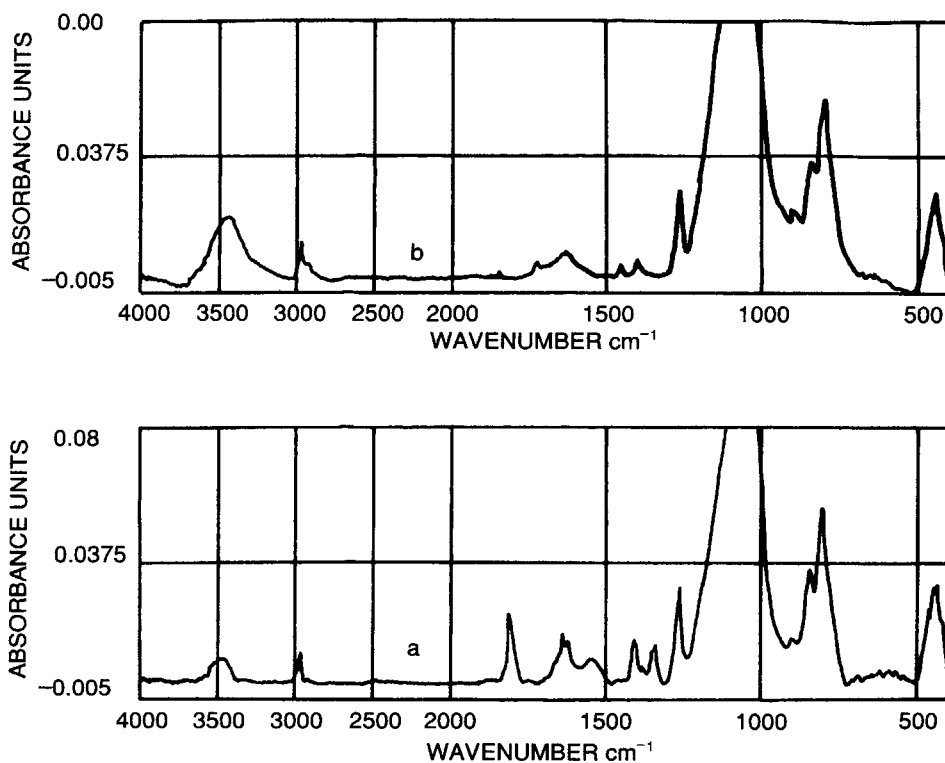


Figure 6 FTIR spectra (a) of plasma-polymerized HMDSO obtained at 1.1 mA/cm² current density, 133 Pa gas-phase pressure, and 0.25 μm layer thickness and (b) of the same polymer treated with ammonia vapor in plasma after deposition.

(Si—CH₃ asymmetric rocking) as compared to the bands at 840 cm⁻¹ [Si—CH₃ stretching in Si—(CH₃)₃ end groups]. Therefore, during plasma polymerization at higher current density, more methyl groups were removed. The increased intensity and broadening of the Si—O stretching band are indications of an elongation of the polymer chain and of high cross-linking.

The thickness (0.25–0.55 μm) of the HMDSO polymer layer obtained in plasma under the specified conditions did not reflect on the FTIR spectra. Therefore, the deposited layer has a homogeneous chemical structure.

The temperature change of the substrate with a deposited polymer layer from 35 to 125°C did not lead to changes in the FTIR spectra of the polymer.

The gas medium pressure, during polymer deposition in glow discharge, strongly influenced the FTIR spectra of the polymer, which led to changes in the chemical composition and the structure of the layer obtained. The FTIR spectra of the polymer were significantly changed within the pressure range 266–106 Pa. Pressure decrease within this range led to the disappearance of the characteristic absorption bands of the polymer: 840 cm⁻¹ (Si—CH₃ symmetric rocking) and 800 cm⁻¹ (Si—CH₃ asymmetric rocking). Only the absorption bands of the Si—O bond (1060 cm⁻¹) and of the Si—H bond (2100 cm⁻¹) remained. This probably reflects the changes both in the chemical composition and in the chemical structure of PHMDSO.

Ammonia treatment of the polymer in glow discharge, which was carried out under the same conditions of gas medium pressure (from 13.3–266 Pa), did not lead to changes in the FTIR spectra, i.e., the additional treatment with ammonia did not change the chemical composition of the polymer. Possible structural changes at the layer surface can occur, but they did not result in changes of the FTIR spectrum of the layer.

Glow discharge polymer deposition in a mixture of the monomer HMDSO and of ammonia vapors during polymerization did not change the FTIR spectra of the polymer obtained, i.e., no absorption

bands due to the creation of new bonds were observed.

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