

Raman investigation of sol-gel-derived hybrid polymers for optoelectronics

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A Raman spectroscopic study was carried out in order to investigate the synthesis process of organically modified silane (ORMOSIL) hybrid polymers. These materials were prepared for optoelectronic application, using the sol-gel technology. Our aim was to analyse the ability of Raman measurements to estimate the efficiency and correctness of particular stages of the technological process.

To synthesise a hybrid for optical planar waveguides, denoted as GSiC, a system of 3-glycidoxypropyl-trimethoxysilane/methacryloxy-propyltrimethoxysilane (GPTS/ MPTS) was used as a precursor. To diagnose the first step – gelation – the Raman spectra of monomers and gel were recorded. Analysis showed that gelation parameters should be improved to increase the efficiency of monomers hydrolysis and epoxy ring opening in GPTS. After next two steps – deposition and hardening – Raman microscopy was used for the characterisation of polymer thin films. Information about the film thickness, opening of double C=C bonds in MPTS and types of bonds in organic and inorganic part was obtained. Raman spectroscopy proved its considerable potential in technological process diagnostics. A molecular structure of components can be controlled at relevant stages of the synthesis. This is necessary in order to design new materials on a molecular level and obtain required properties and good quality of the final product.

Keywords: Raman spectroscopy, optical materials, hybrid polymers, sol-gel.

1. Introduction

The interest in the application of inorganic-organic hybrid polymers – organically modified silanes (ORMOSILs), in electronics and optoelectronics has increased rapidly during last decade. The main reason for this development is wide variety of controllable optical, mechanical and electrical properties which can be easily obtained by proper molecular design of used precursors. By the incorporation of organic components into an inorganic silica network it is possible to combine the advantages of organic and inorganic materials. Hybrids have better thermal stability than organic materials [1,2]. Inorganic compounds also increase the scratch resistance and hardness of material. In comparison with inorganic materials they have better toughness and flexibility. Moreover, their workability is very good. To obtain the required properties of hybrid material, the precise control of its molecular structure must be ensured during the production.

ORMOSILs are used in optoelectronics to produce planar waveguides, lenses, Bragg gratings and components for integrated optics. Moreover, dielectric layers, coatings and packaging are produced from these materials. Research to apply them in optical fibre sensors (including bio-sensors) and solid state lasers is underway [1–5].

ORMOSILs are usually prepared in the sol-gel technology. The main advantage of this method is the possibility of synthesis of sophisticated materials in a relatively simple, cost-effective and low-temperature process. Sol-gel enables precise control of composition and optical and mechanical properties of the final product. This method allows one to connect organic components, which are decomposed in high temperatures, with inorganic ones, which have high thermal resistance. The most important drawbacks of sol-gel technology are: the high cost of some of the precursors and lack of the product resistance to temperatures higher than several hundreds degrees centigrade which manifests itself when the organic part is oxidised and the structure of inorganic one may be changed.

Investigation of the hybrid polymers properties is a very difficult task because of their complicated structure and

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multi-staged synthesis process. On the other hand, a permanent development of optoelectronics in general, and particularly systems based on integrated optics and fiberoptic technology requires new, better materials and, consequently, more advanced systems for control and support of technological process.

Raman spectroscopy can be applied to hybrid polymer characterization and can provide very useful information about chemical structure of components and products as well as direction, correctness and efficiency of the technological process [6]. For the sol-gel, Raman measurements can be used for investigation of various steps from precursor hydrolysis through condensation and film deposition to the production of optical components.

Riegel *et al.* [7] conducted a kinetic Raman investigation of hydrolysis and condensation of 3-glycidoxypropyl-trimethoxysilane/3-aminopropyl-triethoxysilane (GPTS/APTS). The behaviour of the trialkoxysilyl moieties was analysed as well as reactions of the epoxy ring in GPTS. An FT-Raman spectrometer was used with excitation wavelength of 1064 nm. Laser power on sample was at the level of either 500 mW or 1 W. The spectral resolution of 4 cm^{-1} was obtained. The intensity of Raman doublets: 643 cm^{-1} and 613 cm^{-1} for GPTS, as well as 650 cm^{-1} and 627 cm^{-1} for APTS, assigned to stretching vibrations $\nu(\text{Si}(\text{O}-\text{CH}_3)_3)$, was used to investigate the efficiency of hydrolysis. The peak at 1256 cm^{-1} and band at 457 cm^{-1} were used to monitor the epoxy ring opening in GPTS and the growth of siloxane network, respectively. Measurements were performed for different GPTS to APTS molar ratios, amounts of water and temperatures of hydrolysis. The best parameters of gelation for GPTS/APTS system were found.

Li and King [8] compared Raman spectra of gels synthesised from methyltrimethoxysilane (MTMOS)/tetramethoxysilane (TMOS) and 3-(trimethoxysilyl)propyl methacrylate (TMSPM). They investigated the role of organic components in the structure of the sol-gel derived hybrid polymers. Inorganic products of gelation such as siloxane network and simpler structures like Si-OH, trisiloxane rings and tetrasiloxane rings were recognised.

Que *et al.* [4,5] characterised hard coatings $\text{SiO}_2/\text{TiO}_2/\text{ORMOSIL}$ for optical components. Raman peaks at 1350 cm^{-1} (D-band) and 1600 cm^{-1} (G-band), observed for the films heated over 500°C, show the existence of amorphous carbon. For the films heated over 800°C, the D-band shifted to 1356 cm^{-1} and both lines widened, which proves that glassy carbon appeared.

Marino *et al.* [9] made a 2-D mapping of Bragg gratings produced from dye-doped ORMOSILs thin films using Raman microscopy and other methods such as optical microscopy and atomic force microscopy. A two-dimensional mapping was made. The intensity of two Raman peaks was measured. The peak at 1331 cm^{-1} can be assigned to unmodified dye while the peak at 1121 cm^{-1} – to dye molecules modified by a laser beam during the development of the grating. The ratio between area of these two

peaks delivered information about position and shape of the grooves. The period of a few gratings was measured using Raman spectroscopy and results agreed well with those obtained with other methods.

Although it has been shown that Raman spectroscopy can be used on every level of technological process, most papers dealt only with particular problems connected with single stages of process. Such an approach is caused by the complication of the subject of hybrid polymer investigation. It is difficult to work out a complex system for all steps of the process. We think, however, that Raman measurements applied to a complete process are promising and can significantly increase the amount of information obtained.

2. Theory

Raman spectroscopy is based on the recording and analysis of light scattered inelastically by the investigated object [6,10,11]. It can be observed as a result of interaction between monochromatic light and dipoles induced in an oscillating molecule, when the molecule is excited to a virtual state, which does not have to correspond to a real energy level of the molecule. The molecule may return to the initial state and photons in scattered radiation have the same energy as photons of incident light. This is known as elastic Rayleigh scattering. The molecule may also return to the energy level different from the initial one. Photons observed in scattered light may have energy lower than in an incident beam, which is called Raman scattering in the Stokes band. The photon energy greater than in excitation light is related to the anti-Stokes band. The difference between wavelengths of photons in incident (λ_0) and scattered light is known as a Raman shift. It is related to characteristic oscillation frequencies of a molecule. They may be the oscillations of a simple band, as well as of a larger fragment of a polymer network. A particular vibration is Raman active if it is connected with the change in the polarisability tensor of molecule. For the specified excitation wavelength λ_0 , Raman intensity can be expressed as [11]

$$I_R = (I_L \sigma K) P C \quad (1)$$

where I_R is the measured Raman intensity (photons per second), I_L is the laser excitation intensity (photons per second), σ is the absolute Raman cross-section (cm^2 per molecule), K is the constant accounting for measurement parameters, i.e., optical collection efficiency, optical transmission of Raman spectrometer, etc., P is the sample path length (cm), C is the concentration (molecules per cm^3). The influence of the parameter K may be eliminated by comparative measurements.

The analysis of vibrational spectra of hybrid polymers is very difficult because of their complicated chemical structure. Characteristic Raman shifts may depend on neighbourhood of the group of atoms and their position in molecule or polymer network. Additionally also the peaks

assigned to coupling and resonance between a single oscillation may appear in the spectrum.

Selection of the optimal excitation laser wavelength λ_0 is a very important problem in Raman spectroscopy. Intensity of the Raman signal is inversely proportional to λ_0^4 , so if the intensity of Raman scattering is considered, application of VIS or UV laser as the excitation source is more effective than an IR one. However, the fluorescence induced by a laser beam must also be taken to account. The fluorescence is the strongest for the excitation wavelength range 270–700 nm [12], but its influence can be different for various materials, so the excitation in VIS and near UV range may not be appropriate. The efficiency of Raman scattering collection may also depend on the dimensions of investigated structures. Moreover the application of the excitation in UV may be connected with a high price of equipment and the possibility of catalysis of unwanted photochemical reactions which interfere with a technological process. Because of the complication of the theoretical selection, excitation wavelengths in our measurements were chosen in an experimental way, by the comparison of spectra recorded for different excitation wavelengths.

In the case of the investigation of thin transparent dielectric films, a low level of a useful Raman signal [see Eq. (1)] as well as the existence of strong background radiation must be considered. The background signal may come from Raman scattering in the substrate and external radiation.

These problems can be solved if Raman microscopy is used. A laser beam is focused on a very small depth ($\sim\mu\text{m}$) and this allows one to improve the ratio between the intensity of Raman scattering in film and substrate. A high spatial resolution is the main advantage of this technique. However, a very short distance between Raman optics and the investigated film is required in this method. This is the main disadvantage if a future application to *in-situ* measurements is considered.

Alternative methods of thin film measurement are based on the enhancement of Raman effect on the border polymer-noble metal [12] or obtained by using of the total reflection of the laser beam inside the sample [13]. These methods can increase Raman intensity by several orders of magnitude. With these methods the spatial resolution is lower than in Raman microscopy, but it possible to increase the distance between the film and the measuring head.

3. Experimental

3.1. GSiC synthesis

The synthesised polymer is known as GSiC. It belongs to the group of hybrid organic-silicate materials. GSiC was synthesised using the sol-gel technology. In this experiment two precursors: GPTS and MPTS were used for its synthesis. In this system one kind of inorganic and one or two different kinds of organic networks can be created. The chemical structure of GSiC is shown in Fig. 1.

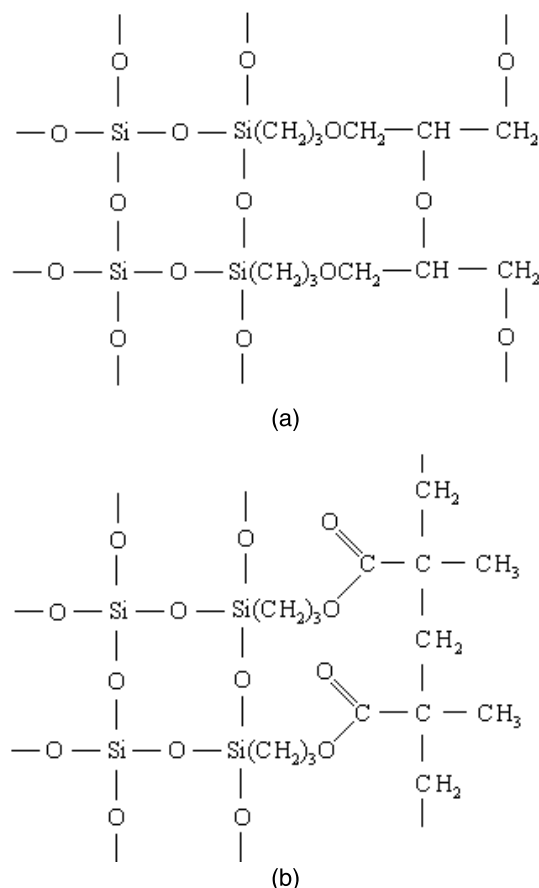


Fig. 1. Chemical structure of GSiC as a product of polymerisation of GPTS (a), polymerisation of MPTS (b).

A multi-step nonhydrolytic-hydrolytic route was used to prepare sol. The system was equipped with a two-neck round bottom flask and a reflux condenser. In the first step, 5.148 ml of Lewis acid SiCl_4 was added to 84.961 g of GPTS to catalyse the epoxy rings opening which is necessary to create the organic network. Reaction should be made in nitrogen atmosphere so, as to avoid the reaction between air moisture and SiCl_4 . The solution was heated up in a silicon oil bath to $+80^\circ\text{C}$ and stirred for 90 minutes. Then, the solution was cooled down to room temperature and 89.24 g of MPTS and 0.38 ml of methanol was added and again heated up to $+80^\circ\text{C}$ and the solution was stirred for another 90 minutes. Subsequently, the solution was cooled down to room temperature. The hydrolysis happened in mild acid conditions. 21.373 g of 0.01 molar HCl was added dropwise to the solution. Slight rise of temperature occurred. The whole system was mixed for 12 hours. The aim was to cause the replacement of the methoxy group by the hydroxyl group followed by the creation of the siloxane structures. The molar ratios of precursor were GPTS: SiCl_4 :MPTS:MeOH: H_2O (0.01 M HCl); 8:1:8:0.21:26.4, respectively. The following day, sol-gel was distilled to remove water and alcohol, which are by-products. Then 2 wt-% of photoinitiator, Irgacure 819 (Ciba) was added to sol-gel and solution was stirred for

4–5 hours. After all the initiator was dissolved, the solution was filtered with the 5.0 μm CN-S -membrane filter.

Gel was deposited and stirred on a BSG (boron-silicate glass) substrate. Films were baked and hardened by the exposition to UV radiation. The process parameters are presented in Table 1.

Table 1. Parameters of thin film deposition process.

Type of substrate	Boro-silicate glass
First step of spin-coating: Rotation velocity (cyc./min.) Time (s)	500 30
Second step of spin-coating: Rotation velocity (cyc./min.) Time (s)	2000 60
Baking: temperature ($^{\circ}\text{C}$) time (h)	130 1
UV exposition Time (s)	
sample No 1	–
sample No 2	100
sample No 3	200
sample No 4	300
sample No 5	400
sample No 6	500
sample No 7	600

Thickness and the refractive index of deposited films were measured with system reflection spectroscopy Filmetrics F20 [14]. The results are shown in Table 2.

Table 2. Thin films' properties

No of sample	Refractive index n	Film thickness (μm)
1	1.54	3.530 \pm 0.001
2	1.52	3.550 \pm 0.001
3	1.54	4.195 \pm 0.001
4	1.53	3.460 \pm 0.001
5	1.52	3.070 \pm 0.001
6	1.50	3.615 \pm 0.001
7	1.50	3.650 \pm 0.001

3.2. Characterisation

Spectra of the precursors and gelation product were recorded with RAMSTAS, a rugged CCD-Raman spectrometer, equipped with a fiberoptic probe using backscattering optical configuration. The system was developed at VTT Electronics [15]. The excitation of 830-nm beam from a semiconductor laser was used. Power on sample was 135 mW, excitation time was 7 s. Measurements were made for the range extending from 200 to 2000 cm^{-1} with the spectral resolution of 8 cm^{-1} . By comparison between Raman spectra of monomers and gel, the efficiency of the most important reactions such as epoxy ring opening and the methoxy group replacement was estimated.

Thin film samples were measured with micro-Raman system Jobin Yvon T64000 [16]. A backscattering optical configuration was used. Measurements were made for the range extending from 200 to 3500 cm^{-1} with the spectral resolution of 4 cm^{-1} . The first task was a proper selection of the excitation wavelength. Three laser beams were tested: 632.8 nm from an He-Ne laser, 488 nm, and 514.5 nm from an Argon-Ion laser. Power on the sample was 4 mW, 7 mW, and 9 mW, respectively. After measurements, the samples were tested by optical microscopy. No trace of damage caused by laser beam was recorded. The main goal of micro-Raman measurements was to determine the molecular structure of films after heating and UV treatment.

4. Results

4.1. Gelation

Characterisation of this process stage can be achieved by the comparison between Raman spectra of precursors and gel. They are shown in Figs. 2, 3, and 4.

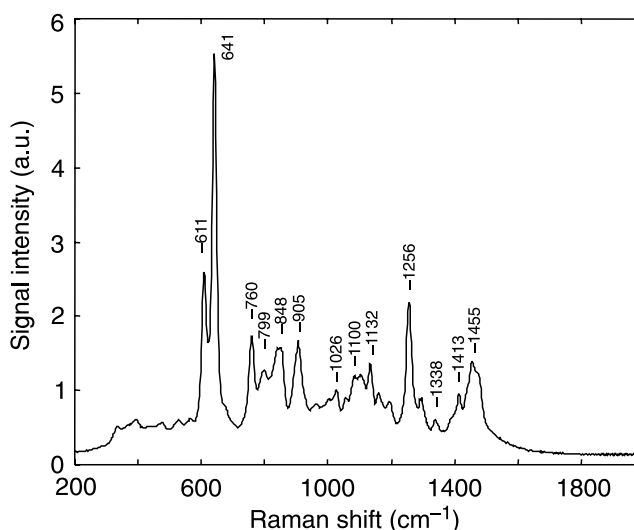


Fig. 2. Raman spectrum of precursor GPTS recorded by RAMSTAS.

The strongest signal in the GPTS spectrum (Fig. 2) is a doublet at 641 cm^{-1} and 611 cm^{-1} which is due to symmetric and asymmetric stretching $\nu(\text{Si}(\text{O}-\text{CH}_3)_3)$. This doublet is characteristic of unhydrolysed trimethoxysilane-molecules [7]. A similar one can be observed for MPTS (Fig. 3) at 641 cm^{-1} and 607 cm^{-1} . Another strong peak in the GPTS spectrum, located at 1256 cm^{-1} is assigned to epoxy ring breaching. Bands at 1455 cm^{-1} and 1413 cm^{-1} are due to symmetric and asymmetric bending $\delta(\text{CH}_3)$, $\delta(\text{CH}_2)$ or $\delta(\text{CH})$. An equivalent doublet for MPTS can be observed at 1455 cm^{-1} and 1404 cm^{-1} . There are also two important peaks at 1640 cm^{-1} and 1713 cm^{-1} in this spectrum which can be assigned to double bonds stretching: the former to $\nu(\text{C}=\text{C})$ and the latter to $\nu(\text{C}=\text{O})$. The rest of the

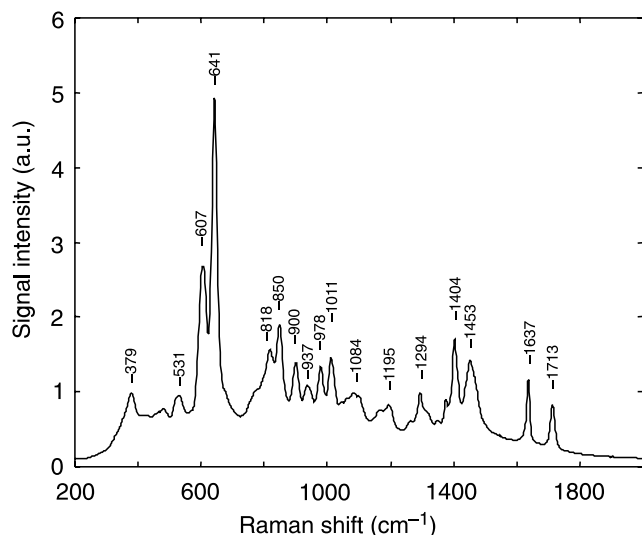


Fig. 3. Raman spectrum of precursor MPTS recorded by RAMSTAS.

peaks can be assigned to different vibrations of organic components [17].

The existence of a still strong peak at 641 cm^{-1} in the spectrum of the gel (Fig. 4) proves that hydrolysis was not effective enough. The intensity of this peak is directly proportional to the total amount of unhydrolysed trimethoxysilane groups. If only one methoxy-group is removed, the molecule no longer contributes to intensity at 641 cm^{-1} [7]. The decrease in intensity of this line is 50%, while for the peak at 602 cm^{-1} it is about 25%, so we may assume that only about 25% of the total amount of precursor molecules were totally hydrolysed while another 25% – partially. To obtain a proper length and homogeneity of inorganic chains in a polymer it is necessary to totally hydrolyse all molecules.

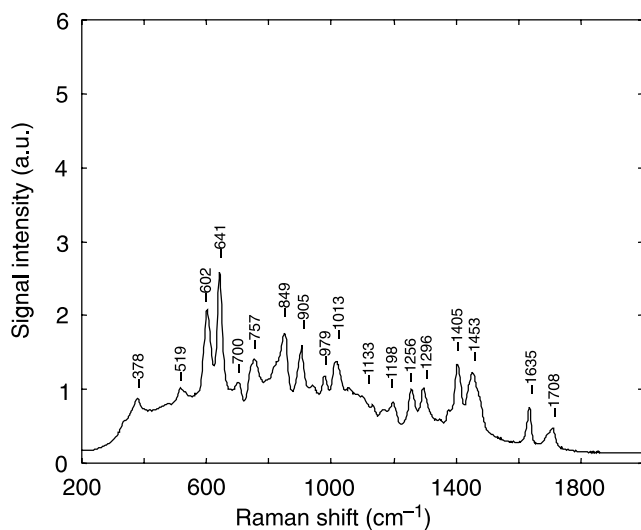


Fig. 4. Raman spectrum of gelation product recorded by RAMSTAS.

In comparison with the spectrum of MPTS, the peak assigned to (C=O) stretching mode (1708 cm^{-1}) is wider and is shifted 5 cm^{-1} towards lower frequencies. A similar change was observed during the hydrolysis of MPTS and hence it indicates the existence of hydrogen bonds in the solution.

Information about the efficiency of the epoxy ring opening in GPTS was obtained from the intensity of the 1256-cm^{-1} peak. It was estimated to be at the level of 50%. Amount of the opened epoxy rings significantly determines properties and homogeneity of this part of organic network which is originated from GPTS.

4.2. Thin films

The Raman signal from substrate was the only one which was recorded when He-Ne laser was used as an excitation source. Although power on sample for $\lambda_0 = 632.8\text{ nm}$ was lower than for other wavelengths, according to Koenig [11], the power level of 4 mW should be appropriate in the case of polymer films. Lack of the signal from thin films was probably caused by the low efficiency of Raman scattering for this excitation wavelength $\lambda_0 = 632.8\text{ nm}$ and problems with focusing of the beam on the sample.

Raman spectra of the polymer films were recorded for excitation wavelength of 488 nm, but the sensitivity of measurements was limited by a strong fluorescence signal.

The comparison between Raman spectra recorded by Raman microscope with the excitation wavelengths 488 nm and 514.5 nm are shown in Fig. 5.

A wide band between 2850 and 2980 cm^{-1} can be observed in both spectra. It is assigned to stretching vibrations: $\nu(\text{CH})$, $\nu(\text{CH}_2)$ and $\nu(\text{CH}_3)$. Another strong peak at 456 cm^{-1} originates from $\delta(\text{Si-O-Si})$ bending [17]. This

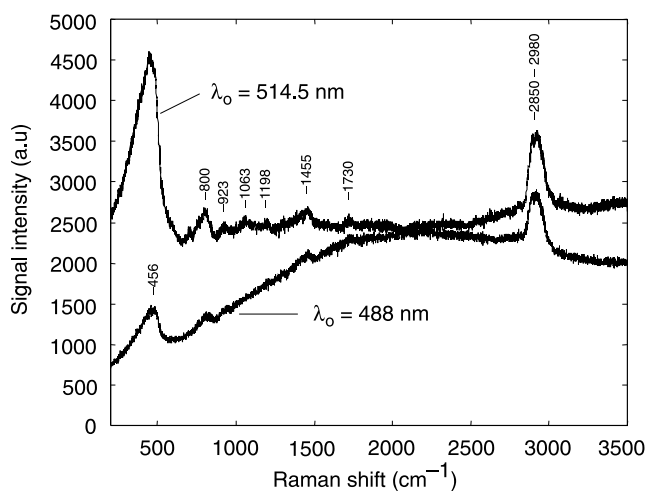


Fig. 5. Comparison between Raman spectra of sample No 1 recorded by Raman microscope with excitation wavelengths λ_0 of 488 nm and 514.5 nm. Time of exposition – 1 min. Notice: Arbitrary units used for micro-Raman result presentation are not the same as these used for RAMSTAS.

peak was also strong in a pure substrate spectrum so, it is very difficult to describe attribute the contribution of inorganic network of polymer to intensity at 456 cm^{-1} . A similar problem occurs for symmetric stretching $\nu_s(\text{Si-O-Si})$.

The weaker band at 1455 cm^{-1} is probably due to asymmetric bending $\delta(\text{CH})$, $\delta(\text{CH}_2)$ or $\delta(\text{CH}_3)$, but deformations of O-CH₂ or scissoring of hydrogen atoms in CH₂ may also contribute to its intensity [17].

The peak at 1730 cm^{-1} can be assigned to (C=O) stretching [17]. Contrary to what was observed for gel spectrum, the intensity of this line is much stronger than of the line assigned to $\nu(\text{C=C})$ (between 1600 cm^{-1} and 1650 cm^{-1}). It suggests that as a result of heating and action of UV radiation the C=C bonds were opened and replaced by single bonds while C=O remained not opened.

The ratio between intensity of bands at $2850\text{--}2980\text{ cm}^{-1}$ and 456 cm^{-1} is higher for excitation of 488 nm than for 514.5 nm . It indicates that the 488-nm laser beam was better focused on the film than the 514.5 nm one. On the other hand, when the 488-nm beam was used, existence of the fluorescence resulted in recording only few weaker peaks. These ones at 923 cm^{-1} , 1063 cm^{-1} and 1198 cm^{-1}

are due to the C-C skeletal vibration, CH₂ vibrations or $\nu(\text{Si-O})$ stretching in inorganic network [17].

Figure 5 shows that it was possible to record more Raman peaks if the excitation wavelength of 514.5 nm was used. Micro-Raman spectra of GSiC thin film samples deposited on BSG are show in Fig. 6.

An estimation of film thickness can be obtained from the ratio of the intensities of the two strongest peaks: $2850\text{--}2980\text{ cm}^{-1}$ (assigned to the organic part of film) and 456 cm^{-1} (the substrate and inorganic part). This ratio is the highest for the thickest sample (No 3) and the smallest for the thinnest one (No 5). A good agreement was obtained with the results of thickness measurements made by Filmetrics F20.

In thin film spectra, the peaks assigned to epoxy ring breaching (1256 cm^{-1}) as well as double C=C bond oscillations (1635 cm^{-1}) were observed only as very weak shoulders. It means that most of the epoxy rings of GPTS and double C=C bonds of MPTS were opened. More than half of the epoxy rings was opened as a result of mixing of GPTS with Lewis acid. It seems though, that some of them were opened also during the next steps of the process. Double C=C bonds were probably opened during stirring baking. There are appropriate conditions to create an organic network. Moieties originating from both precursors behave like a network former. However, there is no proof that a homogeneous organic network was created, because double C=O bonds (1730 cm^{-1}) remained not opened.

Additional Raman peaks at 923 cm^{-1} , 1063 cm^{-1} , 1198 cm^{-1} , 1299 cm^{-1} , 1406 cm^{-1} and 1455 cm^{-1} are due to vibrations in organic network. Most of them have previously been assigned. The peak at 1299 cm^{-1} is due to $\nu_w((-\text{CH}_2)_n)$ wagging [17].

Lack of the peak between 600 cm^{-1} and 650 cm^{-1} suggests that groups of $(-\text{Si}(-\text{O}-\text{CH}_3)_3)$, which remained after gelation, were removed and an inorganic network was created.

No influence of time of exposition for UV radiation on polymer films was observed.

5. Conclusions

Raman spectroscopy proved to be a useful tool of diagnostics of hybrid polymer synthesis process. In this paper, an application of this method to every step of the sol-gel process is presented. During the gelation Raman spectroscopy allowed us to estimate the efficiency of the epoxy ring opening in GPTS and methoxy group displacement in both precursors. For parameters used in the process these efficiencies were at the level of approx. 25–50%. Raman measurements show that a modification of the process parameters is necessary. At present it is possible that unhydrolysed molecules are being removed during distillation or filtration. Consequently, the amount of precursor required for synthesis increases and the price of final product may increase as well. As shown in [7], the efficiency of hydrolysis can be improved to 90% by using Raman measurements to

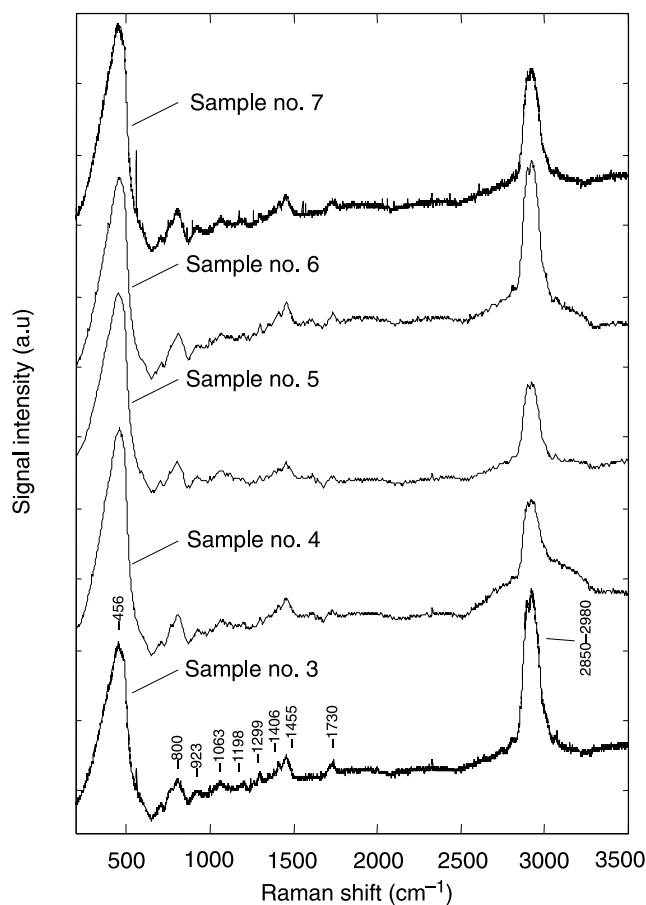


Fig. 6. Comparison between Raman spectra of polymer thin films deposited on BSG (samples 3–7, Table 1) recorded by Raman microscope. Time of exposition – 5 min. For samples No 3, 4, and 5 additional mathematical treatment was applied to reduce noise.

select optimal technological parameters such as precursors' ratio and process temperature.

Thin film measurements have shown that a polymer network was created. The information about its thickness and structure was obtained. It was possible to investigate the efficiency of reactions the most important for network creation such as methoxy group removal, epoxy ring opening and double C=C bonding opening. Results suggest that an inorganic-organic network was created, but probably the organic part is not homogeneous while product of organic polymerisation of GPTS is different than product of organic polymerisation of MPTS.

Investigations presented herein should be treated as introductory ones. Their continuation should increase the amount of the information about the process. The influence of particular technological parameters on process efficiency and product quality must be precisely described. On-line measurements should be made to provide opportunity of process optimisation in real time. As another task, a system for thin film measurement will be developed. This system should be based on signal enhancement obtained on the polymer-noble metal border or by using the total reflection of the laser beam in a sample. It is expected that this configuration should enable thin film measurements *in-situ* during the deposition and following steps.

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