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Raman investigation of hybrid polymer thin films

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Raman spectroscopic studies were carried out for hybrid polymer thin films prepared for photonic applications by the sol-gel technology. Our aims were to analyse the ability of the Raman method to estimate the efficiency of the main reactions of the sol-gel process and to provide information about the chemical composition of the films as well as their thickness, profile, and quality. The difficulties in measurement such as low level of Raman signals, difficulties in data analysis caused by the complex structure of the materials, and the influence of interfering signals, are discussed. The application of Raman microscopy for characterising films based on 3-glycidoxypropyl-trimethoxysilane (GPTS), methacryloxypropyl-trimethoxysilane (MPTS), and 3-aminopropyl-trimethoxysilane (APTES) is presented. The efficiencies of reactions of inorganic and organic polymerisation were measured and their products have been identified. The influence of the excitation beam wavelength as well as the type of substrate on the Raman spectra was investigated. Moreover, two-dimensional Raman mapping enabled us to record the thickness profiles of the deposited structures and to detect their defects.

Key words: *Raman spectroscopy; optical materials; hybrid polymers; thin films*

1. Introduction

A group of inorganic-organic hybrid polymers known as Organically Modified Silanes (ORMOSILs) has been recently developed for photonic applications. These materials are prepared with a sol-gel technology and deposited as thin-film structures. The main reason for developing hybrid polymers is their wide variety of controllable

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optical, mechanical, and electrical properties, which can be regulated by proper molecular design of the precursors used. Hybrids have better thermal stability, scratch resistance, and higher hardness than organic materials [1, 2]. In comparison to inorganic materials, they have better flexibility and a very good workability.

Hybrids can be used in photonics to manufacture planar waveguides, lenses, Bragg gratings, and components for integrated optics. Moreover, dielectric layers, coatings, and packaging are produced from these materials. Research on applying them in optical fibre sensors (including bio-sensors) and solid-state lasers is underway [1]–[7].

Sol-gel manufacturing of hybrid polymer thin films for photonic applications requires high precision, which stimulates the search for effective diagnostic tools. One of them is Raman spectroscopy, which enables the measurement of important chemical and physical properties, including chemical composition, molecular orientation, crystallinity, temperature, and the thickness profile. It also allows the detection of defects. In the case of complex materials such as ORMOSILs, however, Raman investigation of thin transparent films is a difficult task. The applications of Raman microscopy in the investigation of hybrid polymer thin films that have been presented so far include: characterising coatings [4], recording the depth profiles of coatings [5, 6], investigating thin-film materials for waveguide applications [7], and two-dimensional mapping of Bragg gratings produced from dye-doped ORMOSIL thin films [8]. Raman spectroscopic investigation of a sol-gel process covering all steps, from precursors through gelation to thin-film structure deposition and development, has also been reported [6, 7].

In spite of the intensive research conducted in this field, not all ORMOSIL materials and devices have been investigated in a sufficient depth. Moreover, the number of reported Raman optics configurations used in the studies of hybrid polymer thin films [4]–[9] is limited. In this paper, the most important problems of Raman investigations of sol-gel-derived thin films are outlined and the results of selected hybrid polymer film investigations are presented. The main metrological aims of the presented research were to set up an optical system providing a high collection efficiency of the Raman signal from thin transparent films and to select the excitation wavelength and power level of the laser that minimizes interfering signals and does not damage the samples.

2. Raman systems for thin film investigations

Raman spectroscopy is based on the recording and spectral analysis of radiation scattered inelastically by the molecules of the investigated object [9]. As a result of the interaction between monochromatic light and dipoles induced in oscillating molecules, the spectrum of scattered light may contain wavelengths different than those of the incident beam (λ_0). The difference, referred to as Raman shift, is related to the characteristic oscillation frequencies of the molecule, i.e. the vibrations of a single

molecular bond or larger fragment of a polymer network. For a given excitation wavelength λ_0, the Raman intensity can be expressed as [9]:

$$I_R = I_L \sigma K P C \tag{1}$$

where: I_R – measured Raman intensity [photons per second], I_L – laser excitation intensity [photons per second], σ – absolute Raman cross-section [cm^2 per molecule], K – a constant accounting for the measurement parameters, P – sample path length [cm], C – concentration [molecules per cm^3].

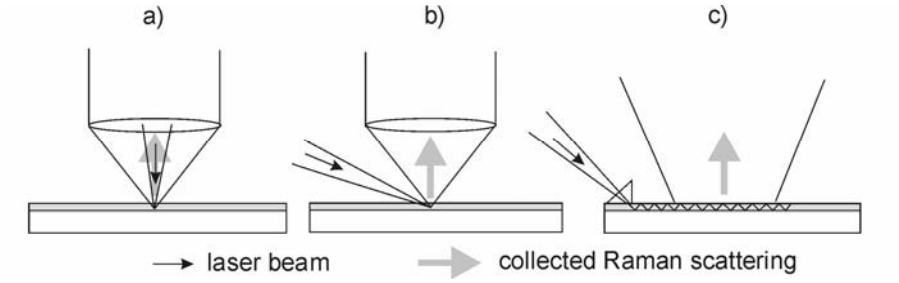

Fig. 1. Optical setups for Raman investigations of thin transparent films: a) the backscattering configuration, b) glancing-incidence configuration, c) waveguide configuration

One of the important problems encountered in Raman investigations of sol-gel derived thin films is a low level of useful Raman signals, which is the result of a small path length P in the sample. Optical setups used in the studies of thin films are presented in Fig. 1. In the most common one – the backscattering configuration shown in Fig. 1a – the angle between the excitation beam, incident on the investigated object, and the collected Raman beam is equal to 180º. However, a typical optical backscattering configuration does not provide sufficient sensitivity when the film thickness is below 10 μm [10]. One solution that can increase the sensitivity of the measurement system is to modify the backscattering setup by using microscope optics. Microscopic systems enable much thinner films to be investigated and provide better spatial resolution (~1 μm) than the typical backscattering configuration (~40 μm) [10]. Moreover, the use of additional pinholes creates a truly confocal system, in which Raman spectra can be recorded as a function of depth [5, 6]. The main disadvantage of microscopic setups is a small distance between the optics and sample (usually a few millimetres), which limits the applications of the setup mainly to *ex-situ* measurements.

The glancing-incidence configuration (Fig. 1b), can be used to increase the effective path length P. This setup, however, is more difficult to adjust as the laser beam must be precisely focused on the sample at the focal point of the collecting optics. Moreover, the efficiency of Raman signal collection depends on the angle between the laser beam and collecting direction [10].

The Raman setup shown in Fig. 1c, referred to as a waveguide configuration, is based on a significant increase of the effective path length P by internal reflection of

the laser beam inside the investigated thin-film structure. The intensity of the Raman signal in the waveguide configuration can be even $3 \cdot 10^3$ times higher than in the typical backscattering configuration [10]. The main drawbacks of the waveguide setup are: moderate spatial resolution and strict requirements of repeatability for launching the excitation laser beam into the thin film structure.

The level of the Raman scattering signal depends on the excitation wavelength. For λ_0 far from the molecule absorption band, the intensity of the Raman signal is inversely proportional to λ_0^4. Therefore, the application of a VIS or UV laser as the excitation source should be more effective than an IR one in terms of Raman scattering. The practical efficiency of Raman scattering versus excitation wavelength, however, may also depend on the dimensions and crystallinity of the investigated structures. Moreover, strong interfering signals originating from laser-induced fluorescence in the organic part of the polymer, Raman scattering in the substrate, and external illumination must also be taken into account. The fluorescence is the strongest for the excitation wavelength from 270 to 700 nm [11] but its level can be different for various materials. As a result, the power and wavelength of the excitation beam as well as the type of substrate must be selected experimentally for each set of the samples.

3. Experimental

3.1. Thin film preparation

Hybrid polymer thin films based on commercially available precursors (3-glycidoxypropyl-trimethoxysilane (GPTS), methacryloxy-propyltrimethoxysilane (MPTS), and 3-aminopropyl-trimethoxysilane (APTES)) were synthesised and investigated. The precursors were mixed with solvents and water and, after distillation and filtering, the obtained gels were deposited and stirred on substrates. Two types of substrates were used for tests: silicon and borosilicate glass (BSG). Films were subsequently baked and hardened. Reflection spectroscopy as well white-light profilometry and prism-coupling refractometry were used to measure the thickness and refractive index of the deposited films. Detailed parameters of the films are presented in Table 1.

Table 1. Investigated thin films

System of silane precursors	Refractive index *n*	Film thickness range [μm]	Thickness determination method	Type of substrate
GPTS/MPTS	1.50–1.54	3.070–4.195	spectroscopic reflectometry	borosilicate glass
GPTS/APTES	1.48–1.50	3–4	white-light profilometry	borosilicate glass
GPTS/APTES	1.48–1.50	3–4	white-light profilometry	silicon

3.2. The Raman system

During the experimental part of the research presented in this paper, thin film samples were measured using a microscopic Raman system, which is shown in Fig. 2.

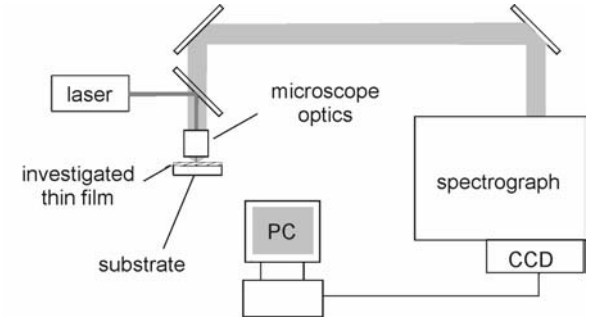

Fig. 2. Micro-Raman system using backscattering configuration

Preliminary investigations were conducted in order to select a suitable excitation wavelength λ_0. Three laser beams were tested on GPTS/MPTS-based thin films: 632.8 nm from a He-Ne laser and 488 nm and 514.5 nm from an Argon-Ion laser. A Raman microscope (Jobin Yvon T64000), equipped with a 100× objective, was used for these wavelengths. Additional tests were carried out on hybrid polymer thin films using an excitation wavelength of 785 nm (dispersive Kaiser Raman Hololab 5000 spectrometer, equipped with an Olympus microscope) and 257 nm (Renishaw spectrometer 1000 UV, equipped with a microscope). The power on samples was a few mW. Beams were focused on the surface of the films. The samples were inspected by optical microscopy after measurements. No trace of damage was observed for excitation in the VIS and NIR ranges, while the application of a UV beam caused photochemical reactions and consequential damage to the samples, which was detected by optical means.

The Raman scattering signal from the substrate was the only one recorded when λ_0 was 632.8 nm or 785 nm, although a power level of a few mW should be sufficient for polymer films [11]. Therefore, an absence of a signal from the film for these excitation wavelengths was probably caused by the insufficient efficiency of Raman signal generation in the polymer structures (as thin as 3–4 μm) and by problems with focusing the beam on the sample.

Raman spectra of ORMOSIL films were recorded for a λ_0 of 488 nm but the sensitivity of the measurements was limited by fluorescence. The spectra of GPTS/MPTS-based films deposited on BSG, recorded by a Raman microscope with λ_0 equal to 488 nm and 514.5 nm are shown in Fig. 3.

A wide band between 2850 and 2980 cm^{-1}, assigned to the stretching vibrations ν(CH), $\nu(CH_2)$, and $\nu(CH_3)$, can be observed in both spectra. Other strong peak at 456 cm^{-1} originates from δ(Si–O–Si) bending mode in the substrate and inorganic

network of polymers [12]. The intensity ratio of the bands at 2850–2980 cm^{-1} and 456 cm^{-1} is higher for the excitation of 488 nm than 514.5 nm. We think that the

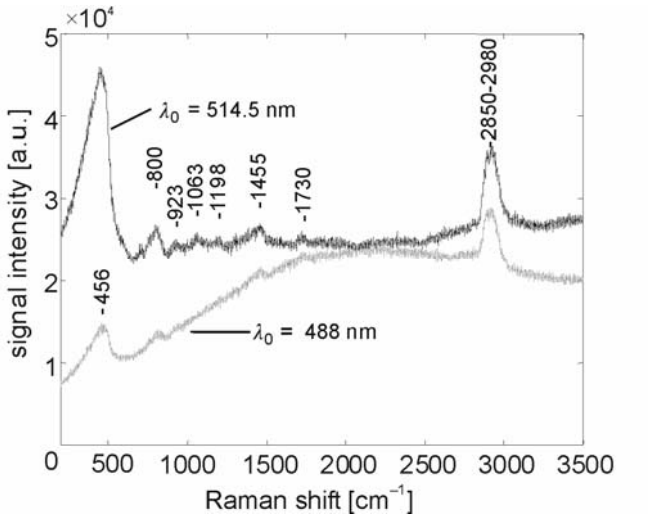

Fig. 3. Raman spectra of samples based on systems of GPTS and MPTS, recorded at various excitation wavelengths λ_0

488 mn beam is slightly better focused on the film than the 514.5 nm one, since it has a smaller diffraction-limited spot size. Due to fluorescence, however, more Raman peaks were recorded for λ_0 equal to 514.5 mm (see Fig. 3), and this wavelength was assumed to be optimal for ORMOSIL film investigations. Measurements were made in the range of 200–3500 cm^{-1} with a spectral resolution of 4 cm^{-1}. A 100× objective was used during investigation of the chemical composition, while a confocal system with a 50× objective and a pinhole with a diameter of 100 μm were sufficient for Raman mapping.

4. Results

4.1. Chemical composition of the films

One of main objectives of the micro-Raman measurements presented in this paper was to determine the chemical composition of sol-gel derived thin films after deposition and subsequent procedures, i.e. heating, hardening, and structure development.

Micro-Raman spectra of GPTS/MPTS thin film samples deposited on BSG are shown in Fig. 4. The strongest bands, at 2850–2980 cm^{-1} and 456 cm^{-1}, are assigned to stretching vibrations (ν(CH), $\nu(CH_2)$, and $\nu(CH_3)$) and δ(Si–O–Si) bending, respectively. The weaker band at 1455 cm^{-1} is probably due to asymmetric bending

(δ(CH), δ(CH_2), or δ(CH_3)), but deformations of O–CH_2 bonds or scissoring of hydrogen atoms in CH_2 may also contribute to its intensity. The bands at 923 cm^{-1}, 1063 cm^{-1}, and 1198 cm^{-1} are due to the C–C skeletal vibration, CH_2 vibrations, or ν(Si–O) stretching in the inorganic network. The peak at 1299 cm^{-1} is due to ν_w((–CH_2)$_n$–) wagging [12].

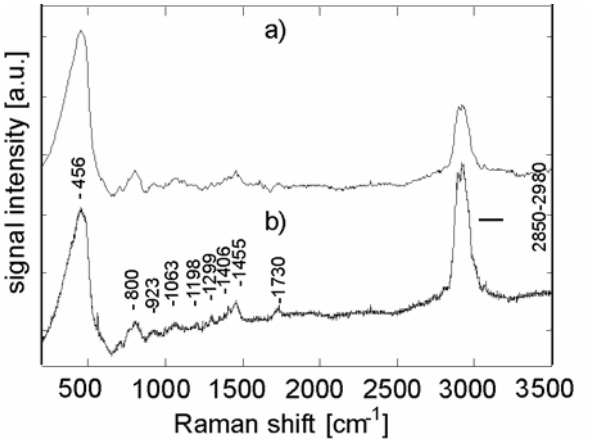

Fig. 4. Micro-Raman spectra of thin films based on systems of GPTS and MPTS; thickness: a) 3 μm, b) 4 μm

In the spectra of investigated GPTS/MPTS-based thin films, the peaks assigned to epoxy ring breathing (1256 cm^{-1}) and ν(C=C) stretching (1635 cm^{-1}) were observed as weak shoulders. The peak at 1730 cm^{-1} is assigned to ν(C=O) stretching. Contrary to that observed in MPTS and sol spectra [7], the intensity of this peak is much higher than the band assigned to ν(C=C). This means that most of the epoxy rings of GPTS and double C=C bonds of MPTS were opened and replaced by single bonds, allowing an organic network to be formed. Moieties originating from both precursors behave like a *network former*. The C=O double bonds of MPTS were not opened and did not participate in network formation.

Regarding other basic reactions in the organic part of various sol-gel derived materials, the following Raman peaks can be important in their studies: 1640–1650 cm^{-1}, assigned to C=N bonds and the doublet at 3310–3370 cm^{-1}, which is due to N–H bonds stretching [12].

4.2. Influence of the substrate

As was shown before, the spectra of thin films may contain peaks originating from the substrate, which may introduce ambiguity in data analysis. One example is the assignment of the peak at 456 cm^{-1} (Si–O–Si network vibrations) in the spectrum of hybrid polymers deposited on a glass substrate. Due to this, the influence of the substrate on Raman measurements was studied by the comparison of the spectra of GPTS/APTES-based thin films deposited on a BSG and silicon substrate.

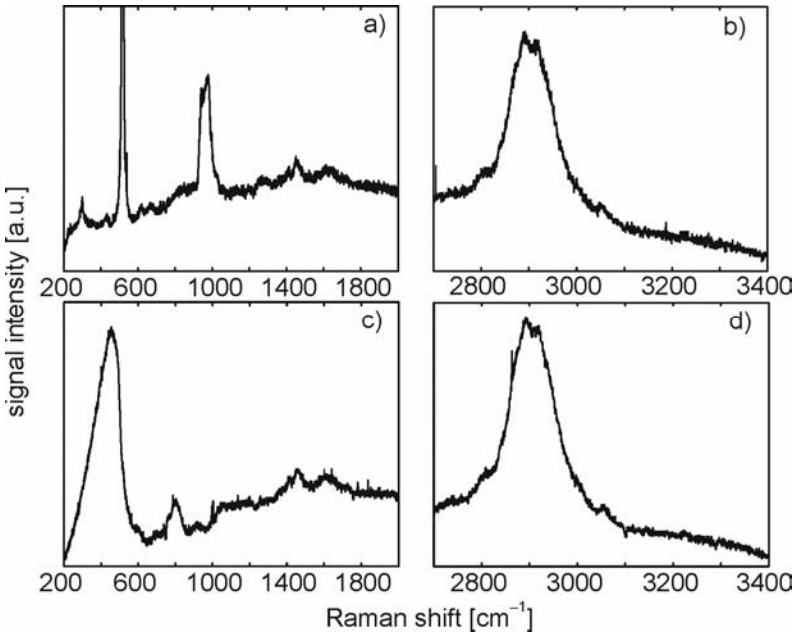

Fig. 5. Micro-Raman spectra of thin films based on systems of APTES and GPTS deposited on: a), b) silicon substrate, c), d) borosilicate glass substrate

The comparison of spectra in Fig. 5 enables the proper assignment of the band at 456 cm^{-1} in the spectra of films deposited on BSG. It can be seen that the SiO_2 network in the substrate is the main origin of this peak for the investigated samples. A small peak at 456 cm^{-1} for films deposited on silicon shows the intensity of the Raman signal originating from the inorganic part of the sol-gel material.

4.3. Profile of thickness

Equation (1) enables thin film thickness to be estimated. For hybrid polymers, this information can be obtained from the ratio of the intensities of the two strongest peaks: 2850–2980 cm^{-1} (assigned to the organic part of the film) and 456 cm^{-1} (assigned mostly to the substrate and partially to the inorganic part of the film). For the example shown in Fig. 4, the ratio is lowest for the thinnest sample (b) and highest for the thickest one (a). Good agreement was obtained with results of thickness measurements made by the spectroscopic system Filmetrics F20. Due to their relative nature, however, Raman measurements can be used to complement profilometry measurements or to monitor changes of the film thickness during manufacturing rather than for absolute thickness measurements. For Raman measurements of thickness, an additional pre-calibration procedure conducted by another method, e.g. spectroscopic reflectometry, is required. Moreover, in practice the dependence of the Raman signal on the thickness may be not linear due to changes in the excitation laser focal tube. In

general, additional calculation must be carried out to take into account the influence of changes of the refractive index at air/film and film/substrate interfaces on the dimensions of the focal tube [5]. In the case of the investigated hybrids deposited on BSG, the difference between the refractive indices of the film and substrate are so low (see Table 1) that despite differences between film thicknesses for various samples, the focal tubes can be assumed to be the same. Consequently, additional calculations are not required.

Additional studies were conducted on using micro-Raman mapping to investigate the thickness profiles of thin films. These measurements could be particularly useful in investigation of integrated optics components. Within the frame of research presented in this paper, Raman images were recorded for planar waveguide structures made from hybrid material based on a system of GPTS/APTES deposited on BSG substrate. Thickness profiles were recorded as two-dimensional distributions of the intensity of the band at 2850–2890 cm^{-1} (assigned to ν(CH), $\nu(CH_2)$, and $\nu(CH_3)$ stretching vibrations). The following investigations were made by Raman microscopy in the mapping mode: structure shape, edge quality, and detection of structural defects.

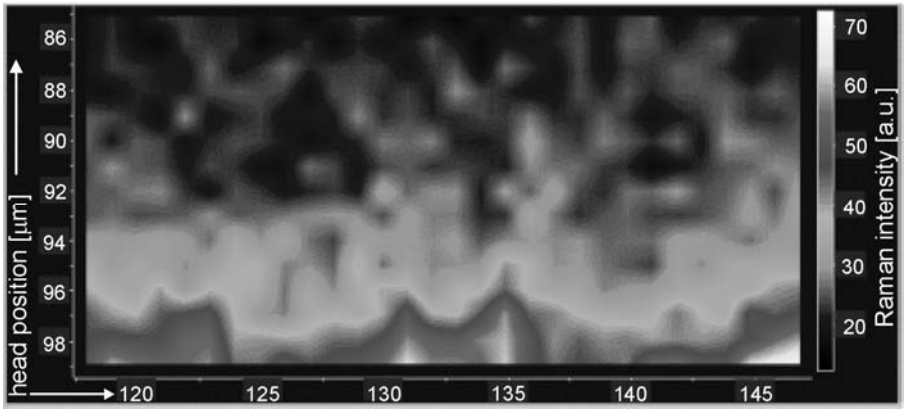

Fig. 6. The image of the edge of an investigated thin-film structure recorded using Raman mapping of the line assigned to C–H bonds

A Raman image of the edge of the investigated waveguide structure is presented in Fig. 6. In the image, the shape of the structure and the thickness distribution are presented by a grey colour scale related to the amount of C–H bonds originating from the organic part of the material. It can be noticed that the edge of the waveguide structure is not sharp and that there are small amounts of sol-gel material outside the predicted area of the waveguide. For photonic applications, the quality of edges may significantly determine the acceptable distance between neighbouring waveguides and cross talks between them.

A Raman image of a waveguide cross-section is shown in Fig. 7. Such a map of the intensity of the Raman band assigned to C–H bonds enables the dimensions and thickness profile of thickness of the path to be determined. Moreover, a defect in the waveguide path

with a diameter of about 2 μm was detected. The results of waveguide dimensions and profile thickness measurements obtained by microscopic Raman 2-D mapping were confirmed by optical microscopy (c.f. Fig. 7) and white-light profilometry. As Raman micro-

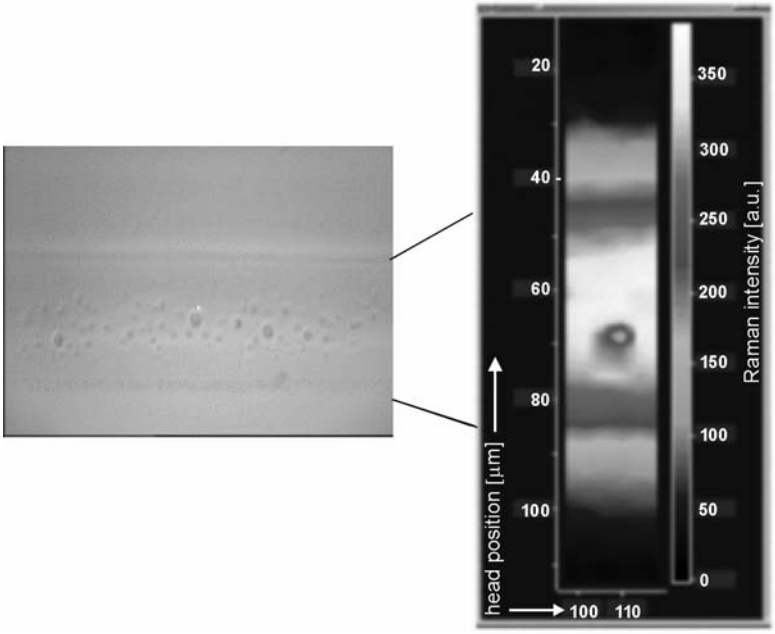

Fig. 7. Microscopic (left) and micro-Raman (right) images
of the cross-section of a sol-gel derived waveguide structure

imaging is based on the detection of chemical bonds (C–H in this particular case), it can be treated as a complementary technique to optical microscopy, spectroscopic reflectometry, and white-light profilomerty, which are all methods that are based on the investigation of optical properties, e.g. transparence, reflectance, and refractive index.

5. Conclusions

Raman spectroscopy proved to be a useful tool in the diagnostics of hybrid polymer thin films. The following Raman measurements were made for thin-film materials based on GPTS/MPTS and GPTS/APTES systems and sol-gel-derived planar waveguide structures: molecular composition and homogeneity, thickness distribution, device shape, structure profile, and edge quality. Moreover, the detection of defects was demonstrated. Good agreement between Raman and other methods of imaging was obtained.

The problems concerning the application of Raman spectroscopy to sol-gel derived hybrid polymer thin films were discussed in this paper. They include: configur-

ing the excitation and collecting optics, selecting the excitation power and wavelength, the influence of the substrate, and data analysis. The comparison of the spectra recorded in various conditions shows that the Raman microscopic measurement system with the excitation laser beam of 514.5 nm and a few mW is an effective tool in investigating sol-gel-derived hybrid polymer thin films thicker than 0.5 μm. *Ex-situ* microscopic investigations presented herein will be the basis for further research. Selecting the optimal wavelength and sufficient power of the excitation beam (subchapter 3.2), studies on the influence of the type of substrate (subchapter 4.2), and analysing optical systems for Raman spectroscopy (chapter 2) will be used during the development of a Raman system for monitoring film deposition and following steps *in-situ*. On-line measurements performed with this system will enable the process to be optimised in real time.

Acknowledgements

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