

*XVII IMEKO World Congress
Metrology in the 3rd Millennium
June 22–27, 2003, Dubrovnik, Croatia*

SOL-GEL MATERIALS INVESTIGATION BY MEANS OF RAMAN SPECTROSCOPY

Marcin Gnyba¹⁾, Małgorzata Jędrzejewska-Szczerska¹⁾, Mikko Keränen²⁾, Janne Suhonen²⁾

¹⁾Gdańsk University of Technology, Department of Optoelectronics, Gdańsk, Poland

²⁾VTT Electronics, Oulu, Finland

Abstract – Raman spectroscopic studies were carried out to investigate the synthesis of hybrid polymers prepared for photonic applications by a sol-gel technology. The main aim was to analyse the ability of Raman measurements to estimate the efficiency and correctness of particular stages of the technological process. Parameters of measurement systems adequate for hybrid material characterisation were found. Dedicated fibre optic system was attached to reaction glass vessel and on-line monitoring was being performed during the first step of the process - gelation. Hybrid polymer thin films, after deposition on technological substrate, were studied by Raman microscopy. Efficiency and time of the most important reactions such as hydrolysis, epoxy ring opening, amine transformation, double bonds opening can be measured as well as thickness of thin films can be estimated.

Keywords: Raman spectroscopy, on-line monitoring, sol-gel.

1. INTRODUCTION

Hybrid inorganic-organic polymers are a new class of materials for photonics, that can be used to produce planar waveguides, lenses, Bragg gratings and components for integrated optics. Moreover, dielectric layers, coatings and packaging are manufactured from these materials. Research to apply them in optical fibre sensors (including bio-sensors) and solid state lasers is underway [1-4].

The main reason for development of hybrid polymers is wide variety of controllable optical, mechanical and electrical properties which can be obtained by proper molecular design of used precursors. By the incorporation of organic components into an inorganic network it is possible to combine the advantages of both groups of materials (e.g. good thermal stability, scratch resistance, material hardness as well as required toughness and flexibility). Moreover, workability of hybrids is very good. However, the precise control of their molecular structure must be ensured during their production to obtain required properties. Unreacted remnants of monomers as well as impurities may significantly decrease optical properties of the material.

Investigation of hybrid polymers, manufactured mainly in sol-gel technology, is a difficult task because of their sophisticated structure as well as a multi-staged synthesis

process. On the other hand, development of photonics in general, and particularly - systems based on integrated optics and fibre optic technology - requires new, better materials and, consequently, more advanced systems for control and support of technological process.

2. EXPERIMENTAL

2.1. Investigated materials

The most important in sol-gel technology alkoxy-silanes and organoalkoxy-silanes as well as materials based on them are the subject of investigations presented in this paper. The list of used monomers includes: tetraethoxysilane (TEOS), 3-glycidoxypropyltrimethoxysilane (GPTS), 3-aminopropyltrimethoxysilane (APTES) and methacryloxypropyltrimethoxysilane (MPTS). During gelation silanes are mixed with solvents and subsequently water is being added dropwise to the solution. Hydrolysis is a first step of inorganic polymerisation while appropriate reactions in organic part enable organic polymerisation. After distillation of by-products and stirring of hybrid material on the technological substrate, inorganic as well as organic network are finally created.

2.2. Measurement systems

Measurement systems are presented in Fig 1. The first step of sol-gel process - gelation - was investigated by Raman systems using excitation wavelength in the range from 720 nm to 1064 nm, thus avoiding the fluorescence induced by a high-power laser beam. The aim was to investigate the hydrolysis and inorganic condensation as well as the behaviour of such groups like epoxy rings, double C=C bonds or NH₂ bonds which take important role during organic polymerisation. The basic devices were CCD-Raman spectrometers, developed at the VTT Electronics [5], equipped with a fibre optic probe. They are using backscattering optical configuration. The excitation wavelength of 830 nm was used for measurements made for the Raman range extending from 200 to 2000 cm⁻¹, while the beam of 720 nm was used for range extending from 2000 to 3900 cm⁻¹. It enabled application of TE-cooled silicon detector, thus simplifying and reducing costs of the system. Spectral resolution of 8 cm⁻¹ was obtained. For various experiments, power on sample from the range extending from 50 to 150 mW was used. Acquisition time,

which determines the time resolution of on-line measurements, was varied from 7 sec. to 5 min., depending on required sensitivity. The proper design of optical system enabled attachment of the spectrometers to the typical glass reaction vessel and performance of remote, non-invasive measurements. Background correction enabled on-line monitoring with presence of external light and consequently – precise control over addition of the ingredients as well as comparison between Raman spectra and viscosity of the material.

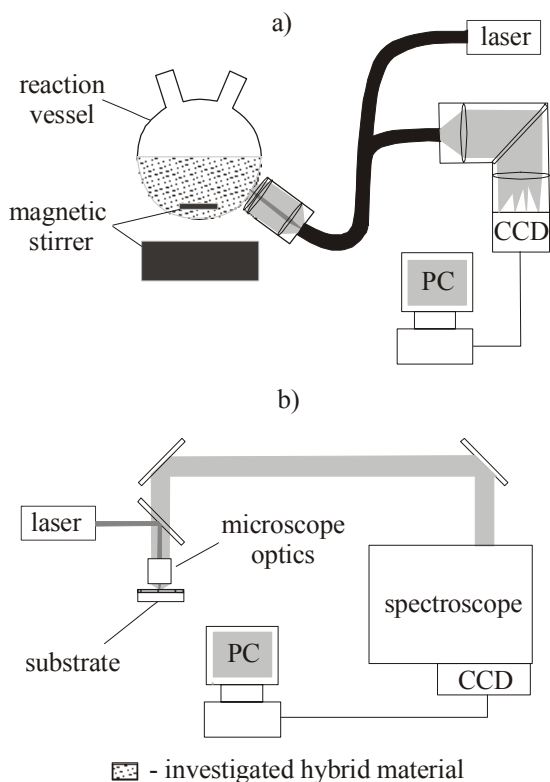


Fig.1. Measurement systems: a) dedicated setup designed for remote control of gelation, b) Raman microscope

The confirmation measurements were carried out using FT-Raman spectrometer FTS 6000. The Nd:YAG laser beam of a wavelength of 1064 nm was used as an excitation source. Power on sample was 450 mW. A liquid-nitrogen-cooled germanium detector was used. Measurements were made in Raman range extending from 100 to 3500 cm^{-1} with the spectral resolution of 4 cm^{-1} .

The main goal of micro-Raman measurements was to determine the molecular structure of hybrid polymer thin films. The micro-Raman system Jobin Yvon T64000 with a backscattering optical configuration was used. After measurements, the samples were tested by optical microscopy. The laser beam of 514,5 nm from an Argon-Ion laser was proved to be the most effective excitation source that prevented the fluorescence induced by a high-power laser beam as well as damages of the sample. For various experiments, power on sample from the range extending from 3 to 9 mW was used. Acquisition time was varied from 3 to 16 min. Measurements were made for the Raman range extending from 200 to 3500 cm^{-1} with the spectral resolution of 4 cm^{-1} .

3. RESULTS

3.1. Investigation of gelation

Regarding inorganic part of hybrid material, intensity of Raman peaks between 600 and 650 cm^{-1} , originated from oscillations of alkoxy groups connected with silicon atoms, can be used for estimation of the efficiency of hydrolysis. The band between 400 and 450 cm^{-1} assigned to SiO_2 network stretching, make a following of the inorganic condensation possible [6,7].

As an example, results of Raman studies of TEOS gelation performed with tetrahydrofuran and water solution of hydrochloride acid are presented in Fig. 2. A peak at 651 cm^{-1} can be assigned to TEOS molecules with four groups ($-\text{OC}_2\text{H}_5$) attached to the atom of silicon.

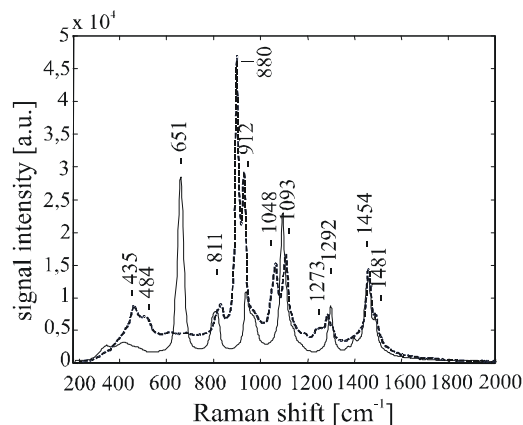


Fig. 2. Raman spectra of TEOS (constant line) and product of its gelation (dashed line).

It can be seen that the band at 651 cm^{-1} totally disappeared in the spectrum of the gelation product. Intensity of this peak shows the amount of non-hydrolysed TEOS, so it can be concluded that efficiency of the hydrolysis was approximately 100%. The appearance of a wide band between 430 and 490 cm^{-1} , that can be observed in spectrum of the product, is due to silane network bending, while a peak at 1049 cm^{-1} can be assigned to Si-O-Si stretching vibrations. It proves that silane network (or at least siloxane structure) was created during the condensation. A strong band at 880 cm^{-1} can be assigned to C-C-O stretching in ethanol. It proves that ethanol is by product of the hydrolysis.

In case of processes based on organoalkoxysilanes, it was more difficult to obtain high efficiency of hydrolysis. An example - gelation of GPTS - is shown in Fig.3.

A doublet at 611 cm^{-1} and 641 cm^{-1} in the spectrum of GPTS is due to symmetric stretching vibrations $\nu_s(\text{Si}(\text{OCH}_3)_3)$ and can give the information about degree of hydrolysis. The strong doublet was also seen in spectrum of the gelation product. Its intensity showed that hydrolysis of GPTS was not successful and less than half of GPTS molecules was at least partially hydrolysed. Any strong signal originated from silane network was not observed.

Regarding organic part of the material, a peak at 1256 cm^{-1} , derived from epoxy ring breathing can be used for investigation of organic polymerisation based on GPTS [6-8]. In case of MPTS, Raman bands at 1643 cm^{-1} and

1708-1730 cm^{-1} , which can be assigned to double bonds: C=C and C=O, respectively, were used for investigation [8].

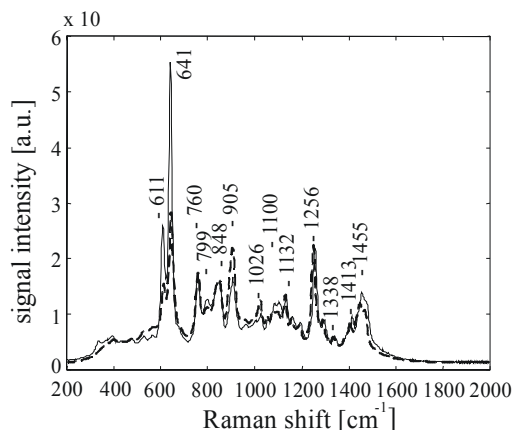


Fig. 3. Raman spectra of GPTS (constant line) and product of its gelation (dashed line).

Raman on-line monitoring enabled optimisation of hydrolysis parameters. Appropriate ratios of silanes, solvents and water as well as time of their stirring, that enable hydrolysis efficiency equal to 100% for system maintained in liquid form, can be measured with high precision.

As an example of the process improved by on-line Raman monitoring, gelation of GPTS/APTES system is presented in this paper.

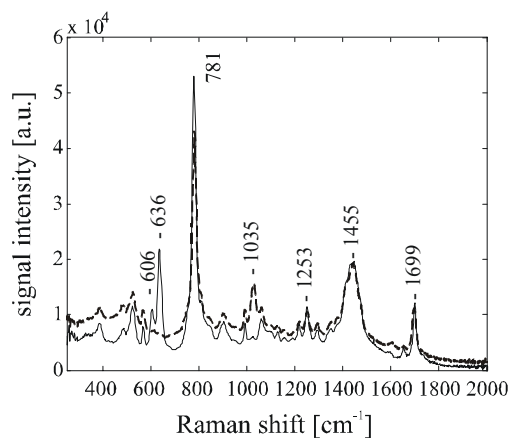


Fig. 4. Raman spectra of GPTS/APTES based solution (constant line) and product of its gelation after 22 hours of stirring (dashed line).

Total disappearance of a doublet at 606 cm^{-1} and 636 cm^{-1} in spectrum of the gelation product shows that efficiency of hydrolysis equal to 100% was obtained much before condensation of network started. A peak at 1035 cm^{-1} can be assigned to methanol that is by-product, while a peak at 1253 cm^{-1} – to epoxy rings of GPTS.

Decrease of main Raman peaks intensity as a function of time of reaction is presented in Fig.5. It can be seen that about 22 hours was required to obtain required efficiency of hydrolysis, while about 25-40% of epoxy rings was opened during this time. On-line Raman monitoring can show the moment when stirring should be stopped to ensure good

parameters of the product for deposition. It prevents the existence of non-hydrolysed alkoxy groups, that can increase optical losses, in the final product. It was also shown that epoxy rings opening is relatively slow process.

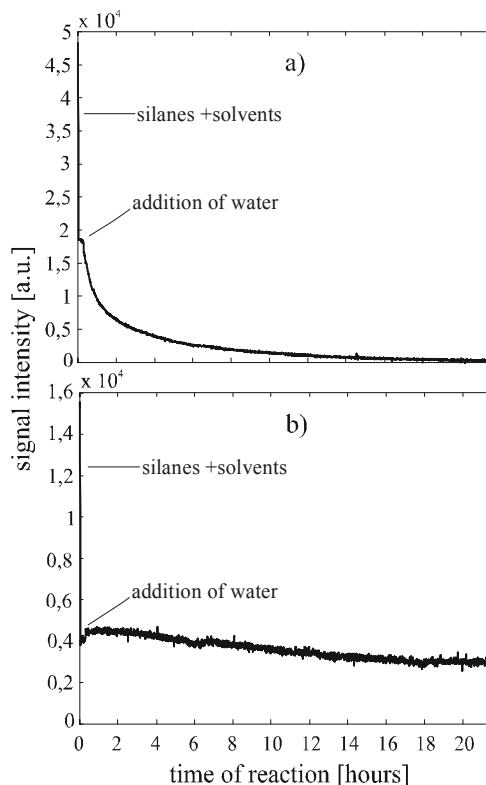


Fig. 5. Decrease of intensity of selected Raman peaks during gelation of GPTS/APTES system: a) 637 cm^{-1} , b) 1253 cm^{-1}

A doublet at 3361-3380 cm^{-1} and 3290-3320 cm^{-1} , assigned to asymmetric and symmetric NH_2 stretching respectively, enabled investigation of the primary amine transformation[8]. It was shown in Fig.6

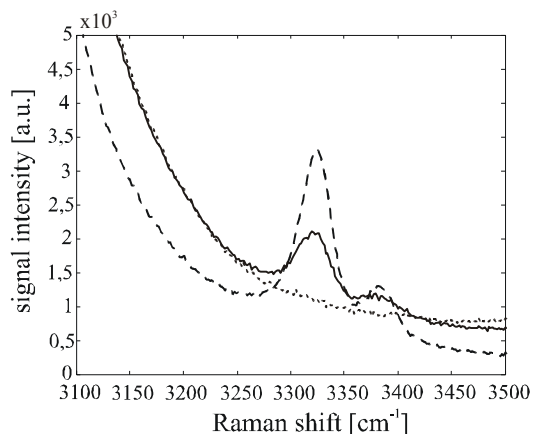


Fig. 6. Decrease of a doublet assigned to NH_2 stretching during gelation of GPTS/APTES system: set of silanes (dashed line), solution after addition of solvents (constant line), system about 2 minutes after addition of water (dotted line).

However, kinetic Raman measurements showed that, during gelation of GPTS/APTES based system, epoxy ring opening is significantly more slowly process than amine

transformation and consequently it was proved that amine-epoxy reaction does not proceed as rapidly and efficiently as it was expected.

Obtained results were confirmed by FT-Raman measurements of the precursors and products.

3.2. Thin film investigation

As an example of thin film investigation, Raman spectra of GPTS/MPTS based films are presented in Fig.7. Micro-Raman measurements enabled estimation of film thickness. This estimation 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 material) and 456 cm^{-1} (the substrate and inorganic part). This ratio is the higher for the thicker sample (Fig.7.a) and the smaller for the thinner one (Fig.7.a). A good agreement was obtained with the results of thickness measurements made by spectroscopic system Filmetrics F20.

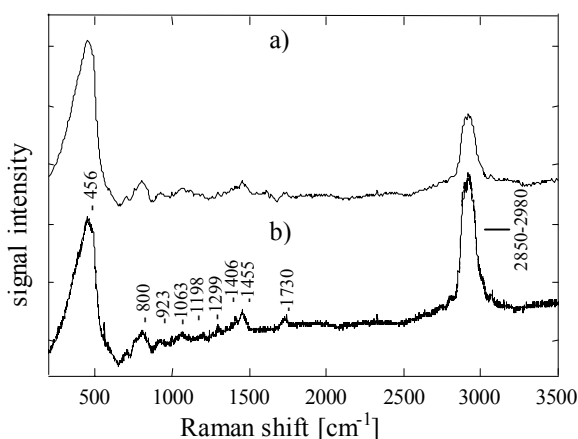


Fig. 7. Micro-Raman spectra of GPTS/MPTS based thin films: a) of a thickness equal to $3\text{ }\mu\text{m}$, b) of a thickness equal to $4\text{ }\mu\text{m}$.

Disappearance of a Raman peak at 1640 cm^{-1} enabled confirmation of the most important reaction which took part during GPTS/MPTS thin film deposition - double C=C bonds opening [6].

A very strong Raman band at $2850\text{--}2980\text{ cm}^{-1}$ assigned to C-H stretching can be used in detection and investigation of these bonds, which are origin of significant losses in NIR range, in organic part of the material.

4. CONCLUSIONS

Raman spectroscopy proved to be a very powerful and versatile technique with a great potential application for hybrid polymer synthesis process. Raman measurements can be applied to investigations for every step of sol-gel process, from the precursors to thin films. The reactions based on most common precursors can be monitored, even if investigated materials are only minor components (10% of volume) of the system. Raman diagnostics should enable improvement of synthesised material properties. As on-line monitoring can bring significantly more information about process, it is necessary to develop systems that enable diagnostics thin film deposition in the real time.

5. ACKNOWLEDGEMENTS

Research were supported by the Technical Research Centre of Finland (VTT), State Committee for Scientific Research (pol. KBN- project no. 4 T11B 019 22) and Gdańsk University of Technology (Faculty of Electronics, Telecommunication and Informatics). We wish to thank to Prof. J. Ulański i Dr. M. Kozanecki from Technical University of Łódź for help in micro-Raman measurements.

REFERENCES

- [1] M. Popall et al., "ORCOMERs - New Photo-Patternable Dielectric and Optical Materials for MCM-Packaging", *48th IEEE Conference Electronic Components and Technology*, pp. 1018-1025, 1998.
- [2] A.B. Seddon, "Sol-gel derived organic-inorganic hybrid materials for photonic applications", *IEE Colloquium on Sol-Gel Materials for Device Applications*, (Ref. No. 1998/412), pp. 6/1-6/6, 1998.
- [3] W. Que, Z. Sun, Y. Zhou, Y.L. Lam, S.D. Cheng, Y.C. Chan, C.H. Kam, "Optical and mechanical properties of TiO₂/SiO₂/organically modified silane composite films prepared by sol-gel processing", *Thin Solid Films*, 359, pp. 178-180, 2000.
- [4] I.G. Marino, D. Bersani, P.P. Lottici, "Holographic gratings in DR1-doped sol-gel silica and ORMOSILs thin films", *Optical Materials*, 15, pp. 279-284, 2001.
- [5] P. Niemelä, J. Suhonen, J. Sumen, J. Aikio, "A rugged raman spectrometer for process measurements", *Proceedings of Finnish Optics Days - Oulu*, p.35, 1998.
- [6] M. Gnyba, M. Keränen, M. Kozanecki, R. Bogdanowicz, B.B. Kosmowski, P. Wroczyński, "Raman investigation of sol-gel-derived hybrid polymers for optoelectronics", *Optoelectronics Review* 10(2), p. 137-143, 2002.
- [7] B. Riegel, S. Blittersdorf, W. Kiefer, S. Hofacker, M. Müller, S. Schottner, "Kinetic investigations of hydrolysis and condensation of the glycidylxypropyltrimethoxysilane /aminopropyltriethoxy-silane system by means of FT-Raman Spectroscopy", *J. of Non-Cryst. Solids*, 226, pp. 76-84, 1998.
- [8] D. Lin-Vien, N.B. Colthrup, W.G. Fateley, J.G. Grasselli, "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules", *Academic Press Inc.*, San Diego, 1991.

Authors:

Marcin Gnyba, Gdańsk University of Technology, Faculty of Electronics, Telecommunication and Informatics, Department of Optoelectronics, ul. Narutowicza 11/12, 80-952 Gdańsk, Poland, phone: +48 58 3472482, fax: +48 58 347 18 48, e-mail: mgnnyba@eti.pg.gda.pl

Małgorzata Jędrzejewska-Szczerska, Gdańsk University of Technology, Faculty of Electronics, Telecommunication and Informatics, Department of Optoelectronics, ul. Narutowicza 11/12, 80-952 Gdańsk, Poland, phone: +48 58 347 13 61, fax: +48 58 347 18 48, e-mail: mjedrzej@eti.pg.gda.pl

Mikko Keränen, VTT-Technical Research Centre of Finland, Kaitoväylä 1, P.O. Box 1100, FIN-90571 Oulu, Finland, phone: +358 8 551 22 34, fax: +358 8 551 23 20, e-mail: mikko.keranen@vtt.fi

Janne Suhonen, VTT-Technical Research Centre of Finland, Kaitoväylä 1, P.O. Box 1100, FIN-90571 Oulu, Finland, phone: +358 8 551 22 98, fax: +358 8 551 23 20, e-mail: janne.suhonen@vtt.fi