INFLUENCE OF SOLVENTS ON UV DEGRADATIONOF POLYSILANES FILMS

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1. Introduction

In the paper we deal with the UV degradation process in polymers in general and silicon based polymers in particular, using thewell-known prototypical polymer poly[methylphenylsilylene] (PMPSi) [1]. Attention is focused on the influence of solventsused for films preparation andon the UV degradation processin these films examined by Photoluminescence (PL) spectroscopy and Electrochemical Impedance Spectroscopy (EIS).

The goalof the study is oriented on the writing of information into thin polymer films and production of nano masks for semiconductor industry [2-4]. PMPSi is a prototypical silicon-based polymer from the polysilanes (PS) group that attracted attention because of their nonlinear optical and photoelectrical properties [2].PSconstitute theexample of the rare group of polymers that have σ-conjugated bonding orbitals along the main chain, in contrast to the carbon based polymers, where the π-conjugation of carbonis responsible for their unique properties. A single bonded linear Si chainis more vulnerable to any distortion and/or cutting compared to the double bonded one what makes the material susceptible to degradation by electron beam andUV radiation [1]. Thus, in the field of applications of PS, their degradation properties may be with advantage used e.g. for electron or UV resists in lithography or as UV sensitive macro initiators of chemical reactions [2, 4]. The general accepted mechanism of UV degradation of PS assumes the generation of excitons by deexcitation σ*-σ, which diffusealong the main chain until they are trapped on the most stressed segment with the lowest potential energy and they further strain it and/or cut them in a non-radiative process resulting in strained weak bond and/or dangling bond on the Si-Si chain. The weak bonds thus serve as the defect pool for the scission of Si-Si bonds [4].

For the studyof degradation process, the fluorimetry is a very suitable spectroscopic method because the photoluminescence (PL) excitation and emission spectra depict the quotient of undisturbed Si-Si bonds. Study of the material absorption replenishes information regarding the identification the material structure, as absorption spectra strongly correlate with PL spectra [5]. Typical excitation PL spectra in PMPSi are characterized by two maxima, one at 333±5 nm (due to σ*-σ transition) and the second at 277 nm due to π*-σ transition, as there is a strong π-σ mixing, whereas the emission spectrum, shows maximum at 355±5 nm only. Just this emission is sensitive to UV degradation and we used it throughout of this study [6] [7].

Another method used for the correlation with the degradation is Electrochemical Impedance Spectroscopy (EIS), used for the elucidation of the electron structure in a wide energy range (6 eV) and excessive dynamics (about 6 orders of magnitude) [8]. The method is examining the interaction of the interface polymer – electrolyte, based on the oxidation reduction(O/R) charge transfer current density j between the semiconductor surface

electronswith the concentration $n_s$and O/R couple ofthe electrolytewith the concentration [A], based on the equation [9] [10]

$$j = ek_F n_s [A], \tag{1}$$

where e is the elemental charge and$k_F$is the transfer coefficient. If the external voltage U is applied, the equal shift of the Fermi energyin semiconductor resultsand thedensity of electron states in semiconductor at the Fermi level$g(E_F)$is

$$g(E_F) = \frac{dn_s}{dE_F} = \frac{1}{ek_f [A]} \frac{dj}{dU} = \frac{1}{ek_f [A] R_{ct}} (U). \tag{2}$$

The term $R_{ct} = \left(\frac{dj}{dU} \right)^{-1}$ is accessible to the measurement as a real part of the impedanceas the charge-transfer resistance, characterizing the rate of the charge-transfer process.

The impedance measurements are carried out in a carefully chosen frequency range, where the charge transfer current density j (and corresponding charge transfer resistance R_{ct}) are accessible, giving the concentration of electrons onthe semiconductor surface accessible for O/R chemical reactions and thusdensity of electron states in semiconductor. More detailed information about EIS method is given in [11].

2. Experiment, results and discussion

2.1Experiment

PMPSi films were deposited from the toluene and tetrahydrofuran (THF) solutions, for PL on the quartz substrates and for EIS measurements on the ITO covered glass substrates. A method used for films deposition was spin-coating and the SpinCoater, K.L.M. was used. Resulting thickness waskept constant, approximately at 400 nm for the concentration 3,5 wt% of PMPSi in toluene and in THF, spin coater frequency for both solventswas 10 s^{-1}, the deposition time was 60 s,such prepared films were annealed at 60 °C for 4 hoursin N_2 atmosphere in the Glovebox (Jacomex). The thickness was measure bythe profilometer Veeco DEKTAK 150.For the PL spectroscopy measurements the fluorimeter Jobin-Yvon Fluorolog-3 spectrophotometer, model FL3-22, was used, the degradation was carried out insitu at 335 nm for the degradation time 0-1200s. For EISmeasurements the spectrometer Solartron analytical 1260, was usedwith the measurements frequency in the range 0.1-1 Hz andthe amplitude of AC signal10 mV and the sweep rate for the superimposed dc voltage ramp 10 mV/s.The electrochemical measurements were performed in the electrochemical arrangement with the electrochemical microcell (volume of 100 μl) filled with acetonitrile, built on the ITO coated substrate and measured using three electrode electrochemical cell in the glovebox. As the source of the UV degradation for the EIS served the low-pressure mercury lamp with the UV intensity at the sample surface (2 mW/cm^2) also placed in the glovebox.

2.2 PLS degradation results

The examples of the PL emission spectra before and after 1200s UV irradiation of PMPSi are shown in Fig. 1. At 335 nm wavelength photons cause Si-Si bondsσ-σ*excitation and σ*-σ exciton, its diffusion, breaking and creating the weak Si-Si bonds first on the penetration depth and later in the whole volume. Thus, the PL spectra exhibit a typical

exciton σ*-σ peak with the maximum at about 357 nm. After progressive degradation we can see the shift of the exciton peak towards to shorter wavelengths. This effect is attributed to the shift of the bond breaking to the stronger bonds. The shift is observable for all films independent of typeof solvents.

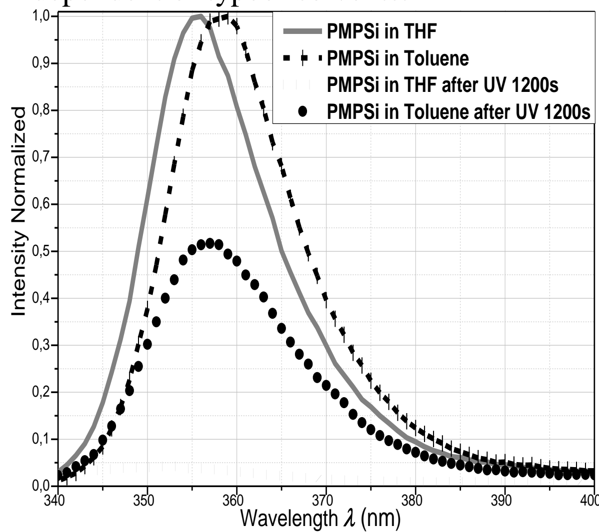

Fig.1:*PL emission spectra of PMPSi prepared in toluene (black dash) and in THF(grey solid)before and after t=1200 s UV(toluene – grey, THF – black dots),λ_{deg}=335 nm,filmsthickness~400nm*

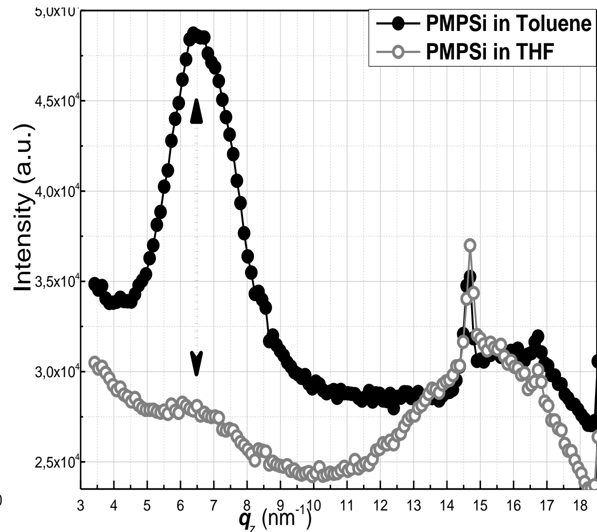

Fig. 2: *X-Ray Diffraction of PMPSiprepared in toluene(black dots) and PMPSi prepared in THF (grey empty dots), samplethickness ~ 1μm*

In the PL emission spectra (Fig. 1) we can observe the effect of solvent used in preparingPMPSi films. There are differences in emission spectra of PMPSi prepared in toluene and THF before and after UV irradiation. PMPSi prepared in toluene degrades with lower rate (black colour)compared toPMPSi in THF (greycolour). The distribution of the chain segment lengths corresponds to the distribution of absorption energies; the longer segment the lower energy of absorption. The excitons move from shorter to longer segments with lower energy and split the weak bonds there.

We assume the solvent has strong influence on the resultingstructure of PMPSi. Toluene is the solvent with a higher density and lower ability to evaporate as THF. We suppose that films made from toluene have betterstructureas films made from THF.This fact was supported by the structure measurements.In Fig. 2 we can seemeasurement of X-Ray diffraction of PMPSi films. The degreeof structural orderis expressedby the intensity ofthe structural peak at q^{-1}=6,5 nm^{-1}; for PMPSifilm prepared in toluene (black line) we can see much more expressed structural peak compared toPMPSi prepared in THF (grey line).We assume PMPSi films prepared in toluene havethe time to create a much more favourable structure with longer conjugation length and less strained bonds compared to that prepared in THF.

2.3 EIS results

The spectroscopic results of the EIS electron structure expressed by the Density of States (DOS) spectroscopy are in Fig. 3. The UV degradation is strongly expressed in the electron structure changes, especially in the DOS distribution near the HOMO region.

For the PMPSi in THFfilmsthe DOS changes by the degradation in the dynamic rangeof 4 orders of magnitude and theenergy span of4 eV. The degradation causes the creation of localized states with the peak about 0.6-0.7 eV above HOMO, corresponding to the decrease of the PL emission peak at 357 nm. The most expressed degradation changes

take place in the energy interval (-1eV, +1eV with respect to standard electrode), where two orders of magnitude growth of DOS is visible for the THF film in Fig. 3 (left), corresponding to thedecrease of PL emission peak in Fig. 1 (grey colour).

On the other hand we cannot see growth of DOS PMPSi in toluene film. The electron structure of these films expressed as DOS in the interval of nearly 6 orders and energy span of 5 eV is obvious and the low figureof the localized states above HOMO is striking (Fig. 3 right). This observationis in accord with a low rate of degradation in PL emission spectra (Fig 1, black colour).

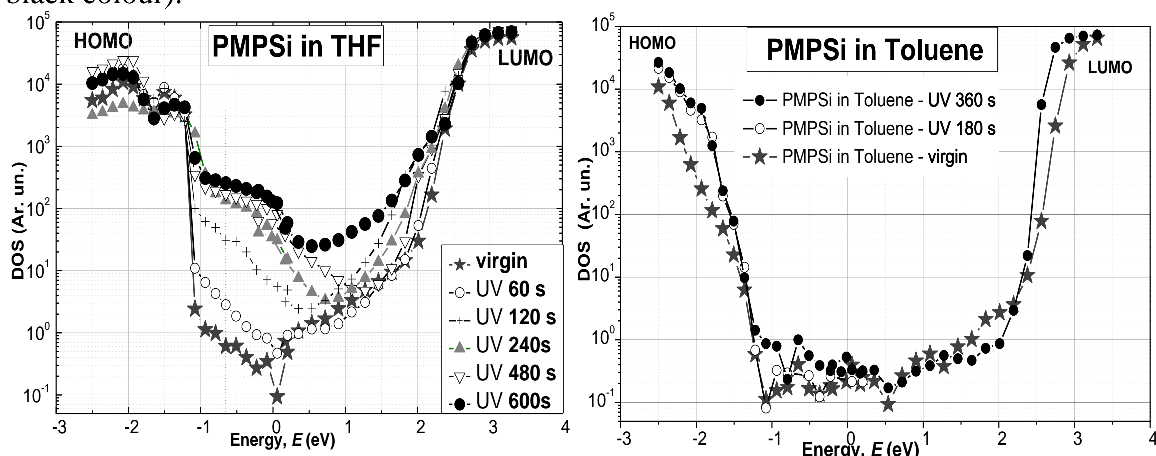

Fig.3:*EIS degradation spectra of PMPSi in THF (left) and PMPSi in toluene (right) before (virgin – stars lines) and after progressive degradation (dots line), films thickness~ 400nm*

2.4 Discussion and conclusions

We elucidatethe scission of the silicone main chain polymer - PMPSi after progressive UV degradation by (PL) spectroscopy and EIS. The exciton peak intensity at about 357 nm was decreasing with degradation time and shifting to the lower wavelength. Degradation resulted in the creating weak (PLactive at 500 nm – not given here) and/or dangling bondsand shortening of the conjugation length of the PMPSi molecule(dangling bond PL not active, but leading to the decrease the exciton peak intensity at 357 nm). The increase of the defects states was observed by EIS and expressed state evolved at about 0.6 - 0.7 eV above HOMO on the films of PMPSi in THF. There is a strong correlation between the increases of the chain defects in DOS measured by EIS with the PL intensity decrease. Striking differencesof results betweenPMPSi films made from toluene and THF solutionin bothspectroscopicmethods after the degradation were observed. The films of PMPSi in toluene exhibit only slow degradation, which is due to the better structure. Differences between PL and EIS measurements were probably caused by the different measurements conditions, as PL degradation was carried out in air ambient, whereas the EIS degradation in N_2 atmosphere of the glovebox.

For nanotechnology applications the use of films prepared by solvent THF is thus distinctlypreferable.

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References:

[1] R. D. Miller, J. Michl: *Polysilanes High Polymers*, Chem. Rev., Vol. 89, pp. 1359-1410, 1989.

[2] S. Nešpůrek, F. Schauer, A. Kadashchuk: *Visible photoluminescence in polysilanes,*Monatshefte für Chemical Monthly, Vol. 132, pp. 159-168, 2001.

[3] F. Schauer, I. Kuřitka, S. Nešpůrek: *UV degradability of aryl-substituted polysilylenes.* Polymer Degradation and Stability, Vol. 84, pp. 383-391. ISSN 0141-3910, 2004.

[4] F. Schauer, I. Kuřitka, S. Nešpůrek: Physics Condens. Matter, Vol. 19, 2007

[5] J. R. Lakowicz: *Principles of fluorescence spectroscopy*, 2nd Ed., Kluwer Academic/Plenum Publishers, New York, 1999.

[6] O. Meszároš, P. Schmidt, J. Pospíšil:*Photooxidation of poly[methyl(phenyl)silylene] and effect of photostabilizers,* Polymer Degradation and Stability, Vol. 91, Issue 3, pp. 573-578, 2006.

[7] F. Schauer, P. Schauer, I. Kuřitka, H. Bao: *Conjugated Silicon-Based Polymer Resists for Nanotechnologies:* EB and UV Meditated Degradation Processes in Polysilanes. Materials Transactions, Vol. 51, No. 2, pp. 197-201. ISSN 1345-9678,2010.

[8] J. Bisquert, F. Fabregat-Santiago, G. Garcia-Belmonte at al: *A review of recent results on electrochemical determination of the density of electronic states of nanostructured metal-oxide semiconductors and organic hole conductors*, Inorganica Chimica Acta, Vol. 361, Science Direct, pp. 684–698, 2008.

[9] Gao Yi Qin, R. Marcus: *On the theory of electron transfer reactions at semiconductor/liquid interfaces. II. A free electron model*, Journal of Chemical Physics, Vol. 113, No. 15, pp. 6351-6360. ISSN 0021-9606, 2000.

[10] N. S . Lewis: *Progress in Understanding Electron-Transfer Reactions at Semiconductor/Liquid Interfaces*, Journal of Chemical Physics B, Vol. 102, pp. 4843-4866, 1998.

[11] F. Schauer, V. Nádaždy, K. Gmucová at al: *Charge Transient, Electrochemical and Impedance Measurements as Tools for Characterization of Nano-Heterostructural Organic/Inorganic Semiconductors*, Nanoscience and Nanotechnology Letters, Vol. 5, Issue: 4, Special Issue: pp. 439-443, 2013.