Analysis of electron beam degraded poly[methyl(phenyl)silylene]

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Polysilanes (PSi) [1] are a broad class of organic materials whose basic building block is a chain built up of silicon. The susceptibility to material degradation is a characteristic property of PSi. PSi are degradable for example by ultraviolet (UV) radiation [2] or by electron beam (EB) [3]. The degradation of the material decreases intensity of luminescence. Poly[methyl(phenyl)silylene] (PMPSi) was selected as a typical representative of PSi.

A cathodoluminescent (CL) device [4] developed in our laboratory was used for study of PMPSi. For the PMPSi measurement, EB energy of 10 keV was used. Detection in the synchronous mode was used to eliminate the influence of the background and of the noise. The modulation frequency was 1 kHz. PMPSi was applied on the silica glass substrate in thickness of 3 μm and covered with an aluminium film. A Nicolet 400 FT-IR spectrometer was used to identify material changes caused by the EB degradation. For infrared (IR) absorption measurements the PMPSi samples remained uncovered.

The decrease of the CL intensity of PMPSi with irradiation time in the semilogarithmic graph (Fig. 1) was attributed to material degradation. The curve is represented by a multi exponential fit and indicates the complexity of the degradation process. The partial regeneration of the intensity, after leaving the specimens in a vacuum chamber of the CL device at room temperature without excitation, indicates the creation of metastable states.

The IR spectra of PMPSi (Fig. 2) support the idea of Si-Si bonds deformation in the main chain of the material during the EB degradation. The EB irradiation of PMPSi leads to the creation of the weak bonds (WBs) in early stages of the degradation followed by the scission of Si - Si bonds and the formation of silyl radicals. The scission of Si - Si bonds is proved by new absorption bands in the IR spectra after exposure of EB degraded PMPSi to air and moisture. The decrease of the CL intensity is a consequence of a Si-Si bond deformation. The partial regeneration of the intensity was attributed to the reverse recombination reactions of silyl radicals in a vacuum and to the recovery of the WBs.

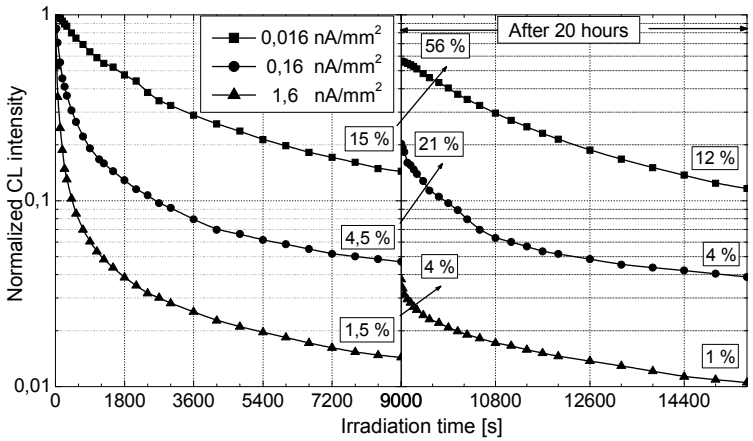

Fig. 2. Decrease and regeneration of CL intensity of PMPSi

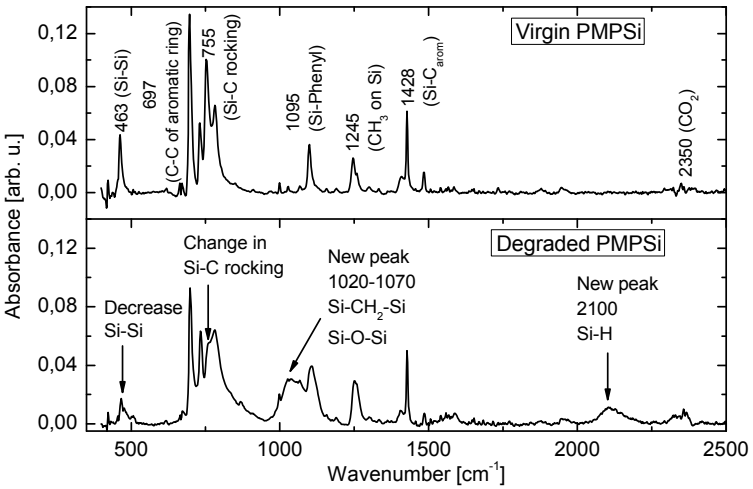

Fig. 2. IR spectra of PMPSi before and after EB degradation

The degradation of PMPSi decreases intensity of luminescence, which impedes the utilization of the material in organic light emitting diodes. On the other hand, understanding of the PMPSi degradation mechanism is important for using PSi as resists in EB lithography.

References:
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Acknowledgements: This work was supported by the grant No. IAA100100622 of the Grant Agency of the Academy of Sciences of the Czech Republic.