

## Cathodoluminescence study of electron beam formed defects in polysilanes

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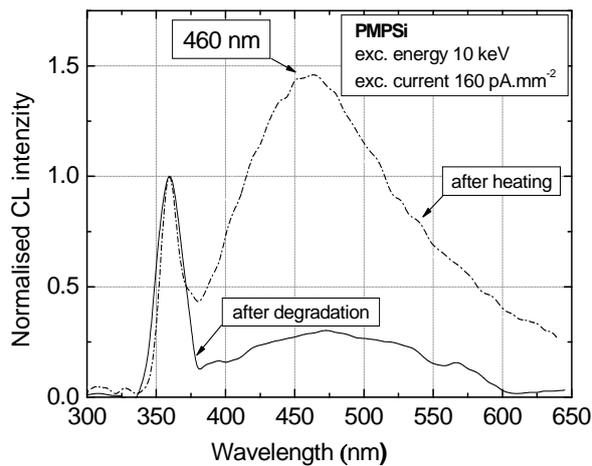
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Keywords: cathodoluminescence, electron beam degradation, poly[methyl(phenyl)silane], PMPSi, silicon polymers

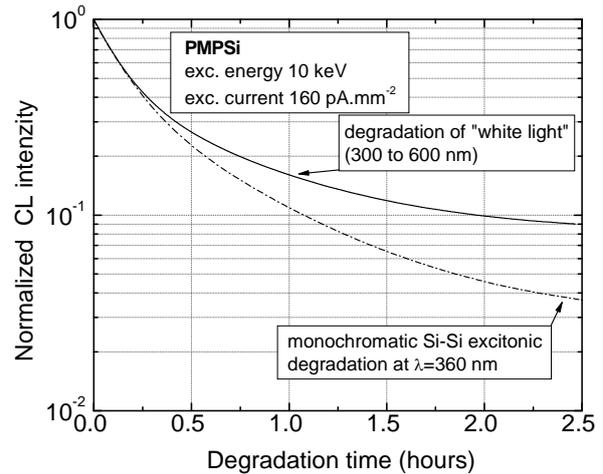
In materials science and semiconductor engineering, cathodoluminescence (CL) is a very efficient tool for the study of electronic substance structure and application possibilities. In spite of this, CL is only very rarely used for investigation of polymers. Recently Wellman et al [1] introduced CL as an important tool for the investigation of materials for organic electroluminescence devices. It is evident that CL may become a strong tool for the investigation of polymer light emission possibilities as well as for investigation of triplet harvester organic solar cells. Our interest has been focused on the group of polysilanes (often also called polysilylanes), especially on poly[methyl(phenyl)silane] (PMPSi), having linear backbone of linked silicon atoms. Cathodoluminescence study of electron beam formed defects in PMPSi is presented in this paper.

Modular CL equipment [2] based on small TEM and completely rebuild in our laboratory was used for the study of PMPSi. A specimen of PMPSi was positioned at the face of a light guide, and the CL emission was collected from the substrate side of the specimen. At the CL spectra measurement, the emitted light was guided to the entrance slit of the spectrometer, and the PMT was positioned at the exit slit of the spectrometer. The equipment was controlled by a PC using the IEEE-488 bus. The studied PMPSi was prepared by the Wurtz coupling polymerization [3]. The low-molecular weight fractions were extracted with boiling diethyl ether. The layers for the CL measurements were prepared from a toluene solution by casting on quartz disk substrates. For electron beam experiments the PMPSi specimens were covered with Al sputtered film of 50 nm.

In Figure 1, the comparison of CL emissions spectra of PMPSi just after 10 minutes of degradation using electron beam energy of 10 keV and beam density of 160 pA.mm<sup>-2</sup> (solid line) and CL emission spectrum of the same sample after subsequent heating to 120 °C (dot dash line) is shown. Both spectra have been measured at room temperature, and the curves have been normalized to their peaks at 360 nm to emphasize changes in the visible spectral region. The main difference in photoluminescence and CL spectra are their long wavelength parts broadly distributed in several pronounced bands, spread in the interval from 400 to 600 nm. These bands are sometimes called the white luminescence region, as they are responsible for the white light emission, prospective for applications. As is shown in Figure 1, CL induces and/or excites predominantly 420-470 nm band. The corresponding change of the CL spectrum due to heating to 120 °C, is most probably due to the thermo-chromic effect and corresponding conformational transformations changes caused by heating. The decisive proof of the defects creation during the degradation process is visible from



**Figure 1.** Cathodoluminescence (emission) spectrum of PMPSi after 600 s of the electron beam degradation (solid line), and after subsequent heating to the 125°C (dot dash line). Measured at room temperature.



**Figure 2.** Degradation kinetics of PMPSi at room temperature measured spectrally unresolved as broad band emission (solid line), and measured at the wavelength of 360 nm (dot dash line).

the kinetics of the weak bonds and/or conformational transformations defects formation in Figure 2, where the dot dash line curve is measured at the excitonic wavelength of 360 nm, whereas the solid line curve depicts the CL measured integrally over the region from 350 to 600 nm. The difference of the intensities corresponds to the weak bonds and/or conformational transformations defects formation.

Comparing these results of electron beam degradation of PMPSi to that of UV degradation [4], some conclusions can be done. The main step of both is the creation of  $^1(\sigma, \sigma^*)$  excitons and their recombination, resulting in Si-Si cutting and dangling bonds creation. The obvious difference in both degradation processes is given by the different penetration depths of both radiations and the different proportion of singlet to triplet excitons in both excitation processes. Electron beam degradation gives rise predominantly to the conformational transformations and corresponding defects with luminescence situated at 420 - 450 nm band, similar to thermochromic conformation changes. Both weak bonds and conformational transformations defects serve as defect pool for Si-Si scission by temperature activated processes. The observed metastability differs in the reversibility, as the electron beam degradation process was reversible, provided certain material specific level of degradation was not exceeded. This observation supports different paths and final states in both UV and electron beam degradations.

We kindly acknowledge the support of the project [5].

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- [5] Work was supported by the Grant No. IAA100100622 of the Grant Agency of the Academy of Science of the Czech Republic.