

Cathodoluminescence as a method for the study of degradation of polysilanes

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Abstract

The paper presents a unique cathodoluminescent (CL) method suitable for studying polysilane properties and the first CL characteristics of the material being investigated. Poly[methyl(phenyl)silylene] (PMPSi) was selected as a typical representative of polysilanes. The PMPSi study is based on the measurement of the intensity of CL emission after passing through the specimen. The major problem of this study is the susceptibility of the material being investigated to the degradation by electron beam. PMPSi degradation strongly decreases the CL intensity. Therefore, detection in the synchronous mode was used to eliminate the influence of the background and of the noise. It was found that the degradation process is partly reversible. A partial recovery of intensity was attributed to reverse recombination reactions of silyl radicals in a vacuum after 20 h of annealing at room temperature. Understanding of the physical and chemical mechanisms of the degradation and of the reversible process of the PMPSi CL emission is interesting for science as well as the application (e.g. resist in electron beam lithography or molecular scale electronic devices).

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1. Introduction

Cathodoluminescence (CL) is the emission of light as the result of electron bombardment. The energy of incident electrons is transferred by secondary electrons and then by excitons to luminescent centres. The emission of light arises from these centres. Electron beam excitation may produce orders-of-magnitude with greater carrier generation rates than the typical optical excitation [1]. This is especially advantageous in studies of wide-band-gap materials. CL is further suitable for thin film investigation because large excitation doses are obtained within a small probe volume. With CL analysis it is possible to assess various properties of a material with spatial resolution of 1 μm

or less. Therefore, CL is an interesting tool for the study of polymer nanolayer behaviour.

The chemical stability of polymers can be influenced by mechanical forces, temperature, chemical catalysis, or high energy radiation. The set of processes leading to the deterioration of some polymer material properties is called degradation. The set of recovery processes of the deteriorated properties under specific conditions is called metastability.

Degradation, in the case of polymers, is mostly associated with chemical bond scission, crosslinking and oxidation of both the main chain and side groups [2]. The produced chemical intermediate can further react and constitute new chemical structures. A reversible chemical reaction is another possibility that leads to recovering broken chemical bonds and, as a consequence, to recovering original material properties. Polymer materials demonstrating such behaviour are very useful for many applications.

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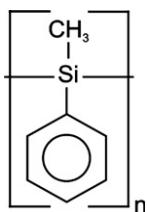


Fig. 1. Chemical structure of poly[methyl(phenyl)silylene] (PMPSi).

Polysilanes are a broad class of organic materials whose basic building block is a chain built up of silicon (Si). The sigma conjugation of sp^3 -hybridized Si atoms in the backbone results in the molecular sigma-orbital delocalization over the entire main chain. The delocalization of sigma electrons over the Si backbone causes the interesting optoelectronic properties of polysilanes [3]. The properties of the material can also be significantly changed or modified by introducing various organic groups or by doping it with various additives. Polysilanes exhibit sharp photoluminescence (PL) with high quantum efficiency in a solid state as well as in a solution. The use of polysilanes as emissive materials in active optical devices is attractive since they can emit light in the range from the ultraviolet to the visible regions [4]. A typical representative of polysilanes is poly[methyl(phenyl)silylene] (PMPSi) (Fig. 1).

Irradiation-induced changes in polysilanes were studied using several techniques, among them were optical absorption [5], thermal and NMR techniques [6], electron spin resonance [7], transient photoconductivity [8], thermally stimulated luminescence [9], or PL [10]. CL studies of the degradation and of the metastable state formation in PMPSi bring new information and can contribute to arriving at a more compact overview of the problems related to polysilane stability.

2. Experimental method

The CL method of the study of PMPSi is based on the measurement of the CL intensity of emitted light after its

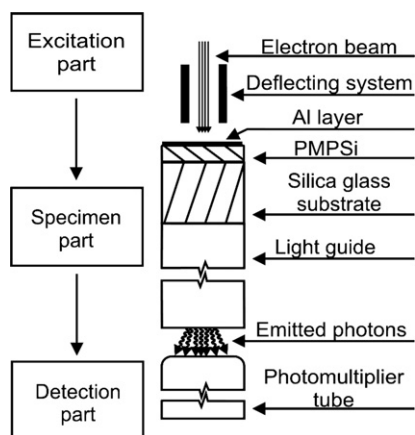


Fig. 2. Layout of the experimental arrangement for the study of CL properties of polysilanes including the specimen part details.

passage through the specimen (Fig. 2). The electron beam, emitted from a wolfram cathode, accelerated and focused in the excitation part, strikes the aluminium (Al) deposited specimen. The emitted photons pass through the specimen and through the silica glass substrate and are guided by a light guide to the detection part. The detection part is based on a photomultiplier tube. The deflecting system modulates the electron beam and enables the excitation, not only in the continual mode, but also in the pulse mode. This is very important for the study of material kinetics as well as for detection in a synchronous mode. CL emission of degradable materials, especially the emission of individual bands, can be very weak. Detection in the synchronous mode can recover signals in the presence of an overwhelming noise and background and can provide high resolution measurement over several orders of magnitude. A dispersive monochromator was used for the measurement of CL spectra. In this case the photomultiplier tube is positioned at the output slit of the monochromator.

The rebuilt transmission electron microscope TESLA BS 242 creates the excitation part. It enables the variation of electron beam energy from 1 to 40 keV. For the PMPSi degradation measurement, electron beam energy of 10 keV was used. The current density of the electron beam was continually alterable. For the synchronous-mode detection the electron beam deflecting system with a blanking diaphragm placed above the specimen was integrated into the equipment. The beam was modulated using the pulse generator TR-0331. The modulation frequency was 1 kHz. The CL emission signal was detected by a Hamamatsu R943-02 photomultiplier tube and measured using a lock-in Unipan 232 B nanovoltmeter. A Carl Zeiss Jena SPM 2 mirror monochromator was used for the CL spectrum measurement.

As follows from the properties of PL [11] (Fig. 3), the emission spectrum of PMPSi consists of two emission bands. The maximum of the weaker broad band in the visible region is located at about 470 nm, whereas the main narrow ultraviolet (UV) band is situated at 356 nm. For this reason the light collection system must be UV trans-

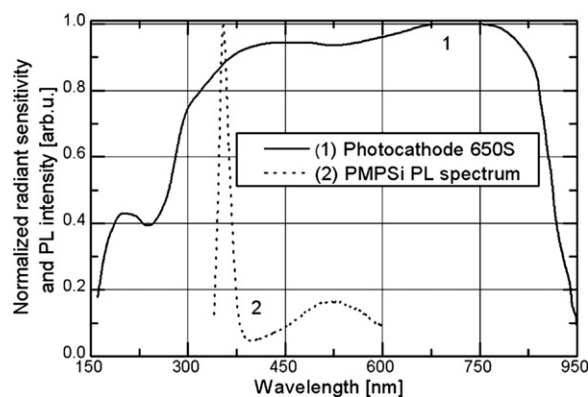


Fig. 3. Typical spectral response of the photomultiplier tube HAMAMATSU R943-02 (1) equipped with GaAs photocathode 650 S compared with the PL emission spectrum of PMPSi (2) [11].

parent to get the highest signal. Consequently, the specimen substrate and the light guide were made of silica glass. The photomultiplier tube with a head-on type synthetic silica window having GaAs photocathode was used. The combination of the GaAs photocathode and synthetic silica window results in high sensitivity over a wide spectral range from UV to IR (160–930 nm) (Fig. 3). The R943-02 features low dark counts and excellent pulse height distribution of single photoelectrons.

3. Specimen preparation

The spin coating technique does not provide sufficient homogeneity of the specimen surface if the PMPSi layer is too thick. Besides, the PMPSi layer should be thin enough to avoid the emitted photon self-absorption. Unfortunately, using electron beam excitation, the PMPSi layer must be thick enough to absorb all impact electrons. Electrons with higher energy have a higher penetration depth as shown in Fig. 4. So, the PMPSi thickness should be optimised for the excitation beam energy as well as for the photon self-absorption. The simulation of the interaction volumes (Fig. 4) as well as of the distribution of absorbed excitation energy in PMPSi (Fig. 5) was accomplished using the program TRANSIT version 2.0, which is based on the Monte Carlo method [12]. The CL gain increases up to the PMPSi thickness of 3 μm for the pri-

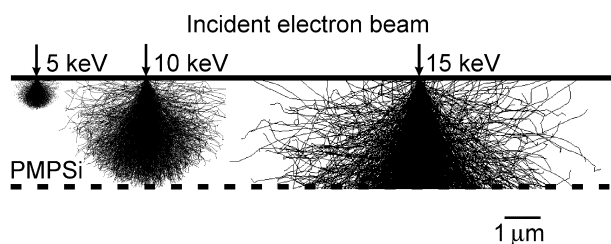


Fig. 4. The Monte Carlo simulations of the electron trajectories in the layer of PMPSi at different energies of the electron beam.

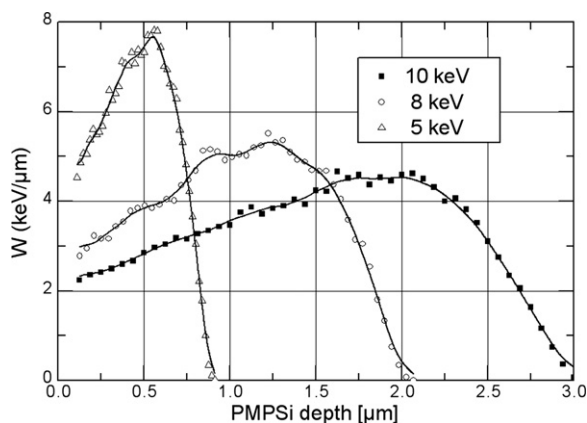


Fig. 5. The Monte Carlo simulation of the absorbed electron energy in the depth of PMPSi at different electron beam energies.

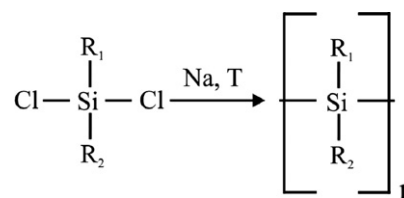


Fig. 6. Chemical synthesis of polysilanes by Wurtz coupling polymerization.

mary electron energy of 10 keV, as is seen in Fig. 5. However, at least 75% of the energy is absorbed up to the thickness of 2 μm. To minimize the losses due to the photon self-absorption and to provide deposition of the maximum electron energy into the material bulk, one should optimize the thickness of the PMPSi layer to 2.5–3 μm at the 10 keV excitation beam energy [13].

The PMPSi material was synthesised, purified and applied on the silica glass substrate at the Institute of Macromolecular Chemistry of the Academy of Sciences of the Czech Republic (ASCR) in Prague. PMPSi was prepared by sodium-mediated Wurtz coupling polymerization (Fig. 6) [14]. The low-molecular-weight fraction was extracted with boiling diethyl ether. The residual polymer possessed a unimodal but broad molar mass distribution [11]. The polymer was reprecipitated from toluene solution with methanol. The layers of PMPSi were prepared from toluene solution by the spin coating technique in two thicknesses (2.29 μm and 3.23 μm). The thicker PMPSi layer approximately corresponds to the proposed optimal thickness of the material. The PMPSi specimens were covered with an Al film by sputtering in our laboratory. The Al film protects the specimen from charging and reflects photons emitted under the specimen surface towards the silica glass substrate.

4. Results of the cathodoluminescence measurement

According to our simulations of the distribution of absorbed electron energy in PMPSi, the layer thickness is important for the detection of a sufficient CL signal. The specimens of the different thicknesses were prepared using two rotating speeds during spin coating (1100 and 750 rpm). The incipient values of the CL intensity prior to the material degradation are given in Table 1 for

Table 1

The values of the CL intensity at the beginning of the electron beam irradiation at the different current densities for two thicknesses of the PMPSi layers. The energy of the electron beam was 10 keV

Layer thickness (μm)	CL intensity (arb. u.)		
	Current density (nA mm ⁻²)		
	0.016	0.16	1.6
2.29	0.47	1.85	17.1
3.23	1.21	6.11	49.5

different current densities of the electron beam. The current density of the beam was changed by modifying the beam current. The irradiated surface has been left identical.

The results of the CL intensity measurement in Table 1 are in good agreement with our simulation. The CL intensity of the thicker PMPSi layer ($3.23\ \mu\text{m}$) was higher, as more energy is absorbed and converted to photons in the thicker layer. The remaining electrons pass through the material into the specimen substrate without the PMPSi excitation. The optimal thickness of the PMPSi layer for the CL intensity measurement is approximately $3\ \mu\text{m}$ at the 10-keV excitation electron beam energy.

The decrease of the CL intensity of PMPSi with irradiation time is plotted in the semilogarithmic graph in Fig. 7. Using the specimen thickness of $3.23\ \mu\text{m}$ the irradiation time dependence of the CL intensity was measured at the different current densities. The irradiated surface was approximately 1.5 mm in diameter. The decrease of the CL intensity is represented by a multi-exponential fit (Fig. 7). The characteristics indicate the complexity of the degradation process. The decrease of the intensity was attributed to material degradation. An interaction of electrons with PMPSi causes the progressive scission of Si–Si bonds in the main chain of the material and leads to the formation of main chain radicals. A series of subsequent reactions of the radicals is possible, which complicates the process of degradation. The strongest intensity is at the highest current density, but in this case the intensity decrease is also the fastest (to 40% after 5 min from the beginning of the excitation). Both the CL intensity and the speed of its decrease decline by reducing the current density.

After 150 min of excitation, the specimens were left in a vacuum chamber of the microscope at room temperature without excitation. After 20 h of such relaxation the specimens were again excited under the same conditions. The partial recovery of the intensity can be seen in Fig. 8. The process of the recovery is the strongest at the lowest

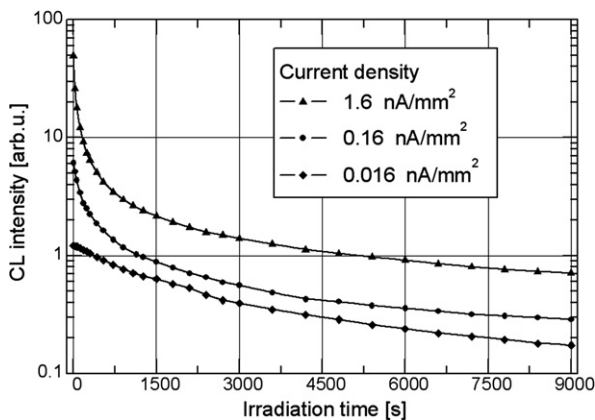


Fig. 7. Decrease of CL intensity with electron beam irradiation time. The specimens were irradiated at different current densities with excitation energy of 10 keV. The thickness of PMPSi layer was $3.23\ \mu\text{m}$.

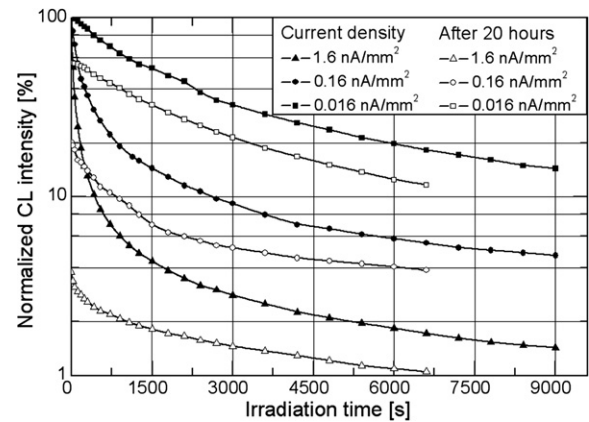


Fig. 8. Decrease of PMPSi CL intensity (full symbols) and the subsequent decrease of intensity (empty symbols) after 20 h of leaving the specimens in the vacuum chamber of the microscope at room temperature. Partial recovery of the intensity is indicated.

current density (about 40%) and decreases with increasing density. No full recovery of the intensity was observed after 150 min of the excitation and subsequently leaving the specimens in vacuum for 20 h.

It was found that the degradation process is partly reversible. A partial recovery of the intensity was attributed to reverse recombination reactions of silyl radicals in a vacuum. In the presence of oxygen, reactions of the cut silicon bonds lead to siloxane formation. During the excitation the polymer chain is stretched and various stages of the Si–Si bond deformation can form. The creation of metastable states as well as the recovery process can be made with the strained and weakened Si–Si bonds.

The CL spectrum of PMPSi (Fig. 9) is in good agreement with the PL spectrum (Fig. 3). The initial spectrum of the previously unirradiated sample is dominated by the narrow UV band with a maximum 357 nm and in addition shows a broad visible band in the range of 420–570 nm. The decrease of the CL intensity with irradiation time is seen in the CL emission spectrum as well. The UV emission

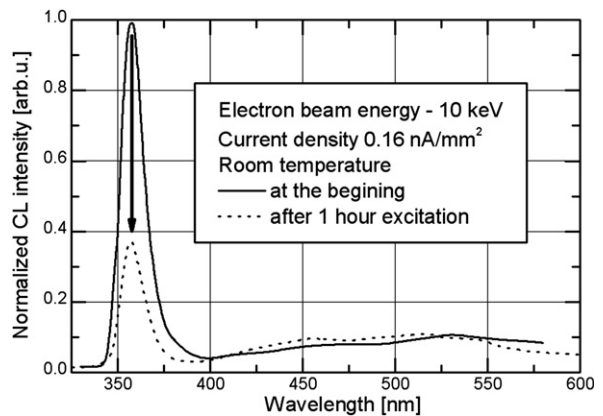


Fig. 9. Change of the CL emission spectrum of PMPSi with electron beam irradiation time.

decreases rapidly, whereas the visible one remains nearly stable during electron beam irradiation. The UV emission is related with the Si backbone (Si–Si bonds). Thus, the decrease of the CL intensity is a consequence of a Si–Si bond deformation. The Si–Si bond scission, crosslinking or weakened bond formation are possible depending on the conditions of excitation.

5. Conclusion

The study of the PMPSi properties using the CL method is complicated by the material degradation, which is characterized by the decrease in CL intensity. The level of degradation depends on the irradiation time as well as on the current density of the excitation beam. This effect impedes the utilization of PMPSi as an emitting, detecting or signaling element. On the other hand, the degradation of PMPSi could be utilized in electron beam lithography.

The recovery of the CL intensity in the absence of oxygen proves the formation of the metastable states in PMPSi. CL investigation of PMPSi has shown the creation of metastable states in the material. The degradation is a reversible process in this case. The understanding of the physical and chemical mechanisms of the degradation and of the reversible process of the PMPSi CL emission is interesting both scientifically and from the application point of view. This knowledge can lead to material stabilization. The recovery process, if fully reversible (the degradation level is less than about 40%), could be applicable in the field of optical memory media or molecular switches.

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