

Degradation of Poly[methyl(phenyl)silylene] cathodoluminescence

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Abstract

The study of the properties of Poly[methyl(phenyl)silylene] (PMPSi) was based on the measurement of intensity of the cathodoluminescent (CL) emission after passing through the specimen. The major problem of the study is the susceptibility of the material investigated to the degradation by electron beam. PMPSi degradation strongly decreases the CL intensity (to 40% after five minutes from the beginning of the excitation). Therefore, the measurement in the synchronous mode was used to eliminate the influence of the background and of the noise. An interaction of electrons with PMPSi causes the progressive scission of weak Si - Si bonds in the main chain of the material and leads to the formation of silyl radicals. A series of subsequent reactions of the radicals is possible, which complicates the process of degradation. It was found that the degradation process is partly reversible. A partial recovery of intensity was attributed to reverse recombination reactions of silyl radicals under the conditions of vacuum after 20 hours annealing at room temperature. Understanding of the physical and chemical mechanism of degradation and of the reversible process of the PMPSi CL emission is interesting from both scientific and application point of view.

Introduction

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 [1]. The produced chemical intermediate can further react and constitute new chemical structures. A reversible chemical reaction is a different possibility which leads to recovery of the broken chemical bonds. This process is related to recovery of the original material properties. Polymer materials demonstrating such behaviour are very interesting for many applications.

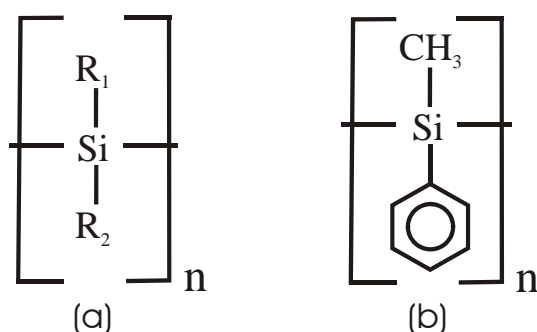


Fig. 1. Chemical structure of (a) polysilanes and of (b) poly[methyl(phenyl)silylene].

Polysilanes (Fig. 1) - broad class of organic materials whose basic building block is chain build up of silicon (Si) substituted by alkyl or aryl groups. Poly[methyl(phenyl)silan] (PMPSi) (Fig. 1) is a typical representative of the polysilanes. The interesting optoelectronic properties of polysilanes are caused by delocalization of σ electrons over the Si backbone [2]. Cathodoluminescent (CL) investigation of PMPSi proved creating of metastable states in the material.

Irradiation induced changes in polysilanes have been studied by several techniques, among them optical absorption, thermal and NMR techniques, electron spin resonance, transient photoconductivity, or thermally stimulated luminescence [1]. 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 of polysilanes stability.

Experimental method

Cathodoluminescence is characterised by light emission under intense 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.

The method of the CL study of PMPSi is based on the measurement of the CL intensity of emitted light after passing through the specimen (Fig. 2). The excitation part of the measurement equipment was arranged using the rebuilt electron microscope. The electron beam, emitted from a wolfram cathode, accelerated and focused in the excitation part, strikes the Al deposited specimen. 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 measurement, not only in the continual mode, but also in the pulse mode. This is very important for measurement in synchronous mode as well as for the study of material kinetics.

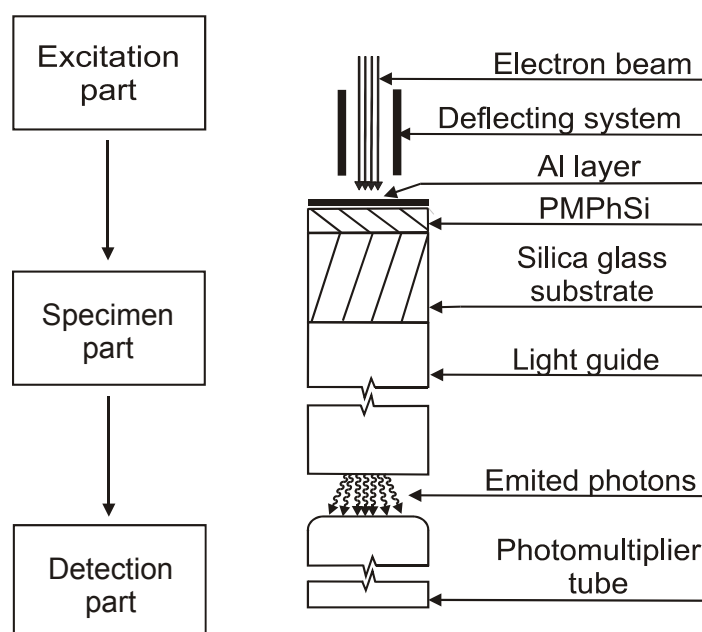


Fig. 2. Layout of the experimental arrangement for the study of cathodoluminescent properties of polysilanes including the specimen part details.

The rebuilt transmission electron microscope TESLA BS 242 constituted the excitation part. It enables variation of electron beam energy from 1 to 60 keV. For the PMPSi degradation measurement the electron beam energy of 10 keV was used. Current

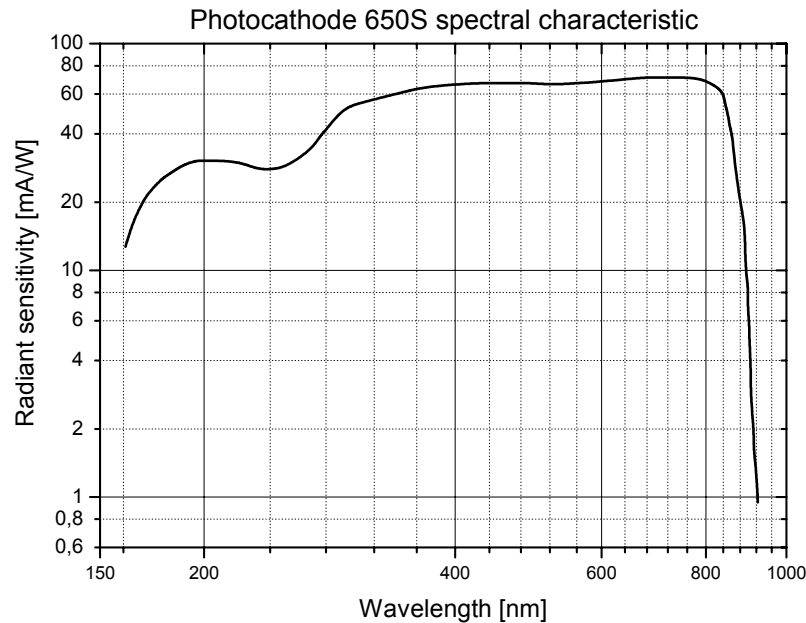


Fig. 3. Typical spectral response of the photomultiplier tube HAMAMATSU R943-02 equipped with GaAs photocathode 650 S. This semiconductor photocathode has negative electron affinity structure and offers high sensitivity from the ultraviolet through near infrared region.

density of the electron beam was continually alterable. For the measurement in the synchronous mode the beam deflecting system with a blanking diaphragm placed above the specimen was integrated into the equipment. Measurement 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. The electron beam was modulated by its deflecting out the diaphragm using the pulse generator TR-0331. The CL emission signal was detected by a Hamamatsu R943-02 photomultiplier tube and measured using a lock-in Unipan 232 B nanovoltmeter. The reference pulse taken from the pulse generator was connected to the lock-in nanovoltmeter.

According to the photoluminescence emission spectrum measurement of PMPSi, the maximum of the weaker broad peak is located at about 470 nm, whereas the main narrow peak is situated at 353 nm [3]. For this reason the light collection system must be UV transparent to get the highest signal. Consequently the specimen substrate and the light guide were made of silica glass. Hamamatsu R943-02 with 51 mm diameter

head-on type synthetic silica window having GaAs photocathode was the photomultiplier tube used. The combination of the GaAs photocathode and synthetic silica window allows high sensitivity over a wide spectral range from UV to IR (160 to 930 nm) (Fig. 3) [4]. The R943-02 features low dark counts and excellent pulse high distribution of single photoelectrons.

Specimen preparation

PMPSi was prepared by sodium-mediated Wurtz coupling polymerization [5]. The low-molecular-weight fraction was extracted with boiling diethyl ether. The residual polymer possessed a unimodal but broad molar mass distribution [3]. The polymer was reprecipitated from a toluene solution with methanol. The thin layers of PMPSi were prepared from toluene solution by a spin coating technique. The material was applied on the silica glass substrate and covered with the aluminium (Al) film. The Al film protected the specimen from charging and reflected photons emitted under the specimen surface towards the silica glass substrate.

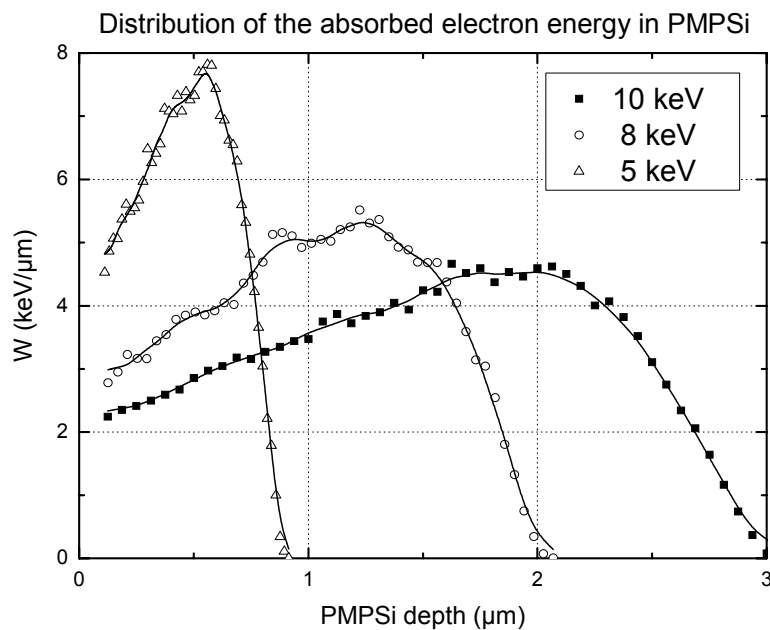


Fig. 4. The Monte Carlo simulation of the depth dependence of the absorbed electron energy in the thin layer of PMPSi.

The CL intensity increases with the thickness of the PMPSi layer up to 3 μm because of the increasing electron energy absorption. The simulation of the absorbed energy distribution in PMPSi was accomplished using the program TRANSIT version 2.0 which is based on the Monte Carlo method [6]. For the primary electron energy of 10 keV at least 75 % of the energy is converted to photons at the layer thickness of 2 μm (Fig. 4). To minimize the losses due to photon selfabsorption, the thickness of the PMPSi layer should be optimized to 2 – 2.5 μm at the 10 keV excitation beam energy [7].

First results

According to our simulations of the absorbed electron energy distribution in PMPSi, the thickness of the layer is important to acquire a sufficient CL signal. The specimens of the different thicknesses were prepared using two rotating speeds of the spin coating technique. There are the incipient values of the CL intensity before the degradation in Table 1. The current density of the beam was changed by modification of the beam current. The irradiated surface has been left identical.

Table 1. The two thicknesses of the thin PMPSi layers were applied on the silica glass substrate using different speeds of the spin coating technique.

Rotating speed (rpm)	Ratio of current density		
	1	10	100
1100	0.47	1.85	17.1
750	1.21	6.11	49.5

The results of the CL intensity measurement in Table 1 are in good agreement with the simulation. The CL intensity of the thicker PMPSi layer (smaller speed of the spin coating) was higher, as more energy is absorbed in the thicker layer and converted to photons. 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 2 – 2.5 μm at the 10 keV excitation electron beam energy.

The fall of the CL intensity in irradiation time is plotted using the semilogarithmic graph. At the excitation energy of 10 keV the irradiation time dependence of the PMPSi CL intensity was measured for the different electron beam current densities as shown in Fig. 5. The synchronous mode eliminated the influence of noise and background and

enhanced dynamic range of the measurement. The frequency of modulation was 1 kHz. The irradiated surface was approximately 1.5 mm in diameter. The current density was increased ten times and then one hundred times.

The strongest intensity is at the highest current density, but in this case the fall of the intensity is also the fastest (to 40% after five minutes from the beginning of the excitation). Both the CL intensity and its fall decrease with decreasing current density. The fall of intensity was attributed to a material degradation. An interaction of electrons with PMPSi causes the progressive scission of weak Si - Si bonds in the main chain of the material and leads to the formation of silyl radicals. A series of subsequent reactions of the radicals is possible, which complicates the process of degradation.

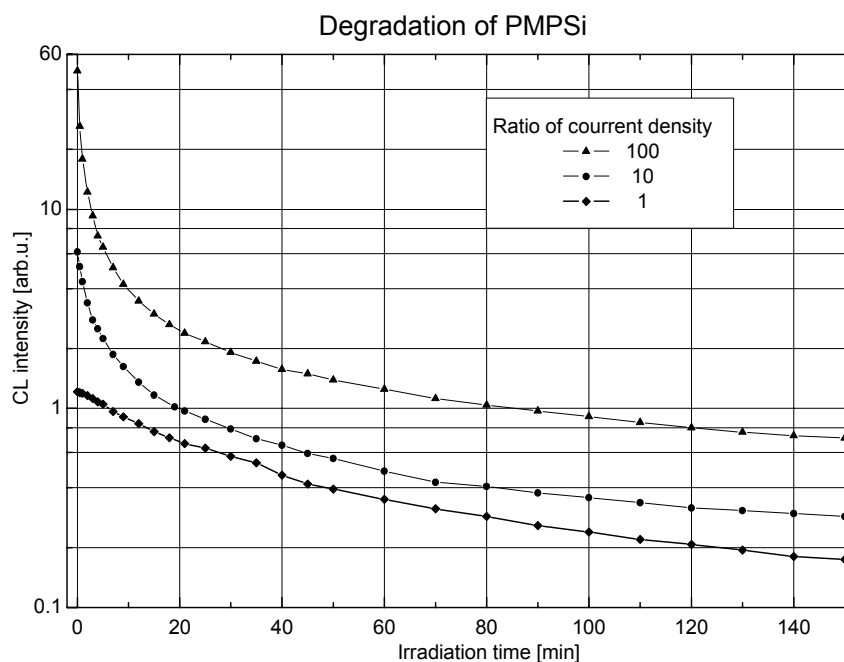


Fig. 5. Fall of CL intensity in relation to irradiation time during electron beam irradiation at different current densities and 10 keV excitation electron beam energy.

After 150 minutes of electron beam excitation, the specimens were left in a vacuum chamber of the microscope at room temperature without excitation. After 20 hours of such relaxation the specimens were again excited under the same conditions. The partial recovery of the intensity can be seen in Fig. 6. The process of the recovery is the strongest at the smallest current density (about 40 %) and decreases with increasing density. No full recovery of the intensity was observed after 150 minutes of the excitation and subsequent leaving the specimens in vacuum for 20 hours.

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 under conditions of vacuum. In the presence of oxygen cut silicon bonds reactions lead to siloxane formation. During the excitation the polymer chain is stretched and various stages of the Si–Si bonds deformation can be formed. The creation of metastable states as well as the recovery process can be related with the strained and weakened Si–Si bonds.

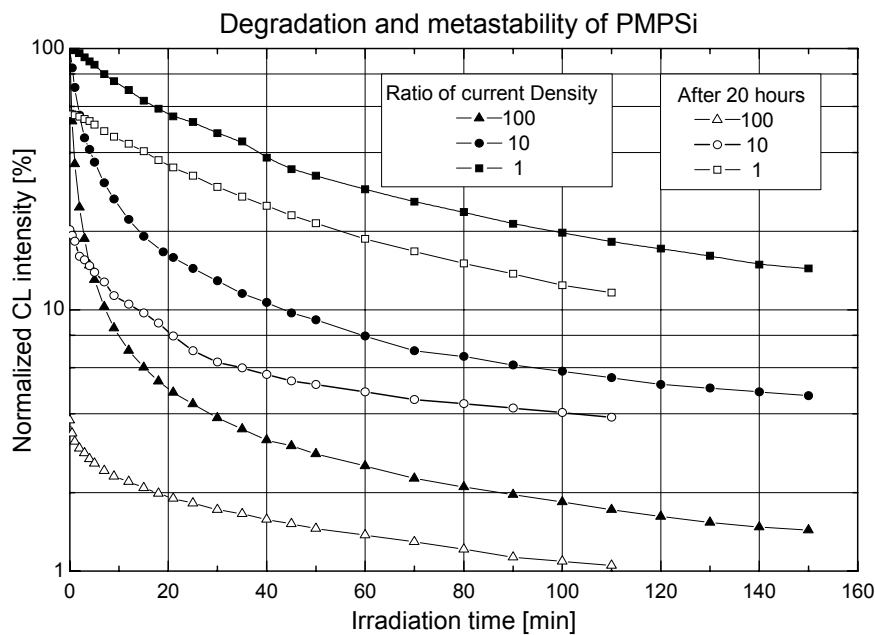


Fig. 6. Fall of the PMPSi CL intensity (full symbols) and the subsequent fall (empty symbols) of intensity after 20 hours of leaving the specimens in the vacuum chamber of a microscope at room temperature, indicating partial recovery of the intensity.

Conclusion

The study of the PMPSi properties using the CL method is complicated by the material degradation characterized by the fall of the CL intensity. The speed of degradation depends on the irradiation time as well as on the excitation beam current density. The effect mentioned impedes the utilization of PMPSi as a detecting or signaling

element. On the other hand, the degradation of PMPSi could be utilized in electron lithography.

The recovery of CL intensity in absence of oxygen proved the formation of the metastable states in PMPSi. The degradation is a reversible process in this case. The understanding of physical and chemical mechanism of the degradation and of the reversible process of the PMPSi CL emission is interesting from both scientific and application points of view. This knowledge can lead to material stabilization. The recovery process could be applicable to optical memory media or to optical sensors.

References

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