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Metastable states in poly(methylphenylsilylene) induced by UV radiation and electron beam

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Abstract

We have examined and measured the density of states (DOS) in a prototypical poly(silylene)-poly(methylphenylsilylene) (PMPSi) using the method of post-transit hole emission signals from traps using the time of flight (TOF) photoconductivity method. The main goal of our measurements was to correlate the metastable states produced both by UV radiation and electron beam and to determine their basic parameters as to their energies and susceptibility for annealing. In the course of measurements we discovered in accordance with our previous observations the fully reversible states around and deeper than 0.55 eV. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Poly(methylphenylsilylene); UV radiation; Electron beam

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1. Introduction

Amorphous silicon and poly(silylenes) are members of the larger class of silicon backbone solids. The latter mentioned backbone polymers are of interest because of their electrical, photo-electronic, and non-linear optical properties. Also, their optical and electrical properties differ from structurally analogous carbon-based π-conjugated systems such as poly(ethylene) or poly(styrene), resembling rather fully π-conjugated systems such as poly(acetylene). The quantum generation efficiency and the charge carrier drift mobility of the order of 10^{-4} cm^2 V^{-1} s^{-1} [1–3], large for organic polymeric photo conductors, stimulated interest in its photo stability and electronic structure. In this paper, we report the measurements of the metastable states produced both by UV radiation and electron beam, and the determination of the basic parameters as to their energies and susceptibility for annealing in a prototypical poly(silylene)-poly(methylphenylsilylene) (PMPSi) using the method of post-transit hole emission signals from traps using time of flight (TOF) photoconductivity.

2. Material properties and experiment

PMPSi (Scheme 1) was prepared by Wurtz coupling polymerization, as described by Zhang and

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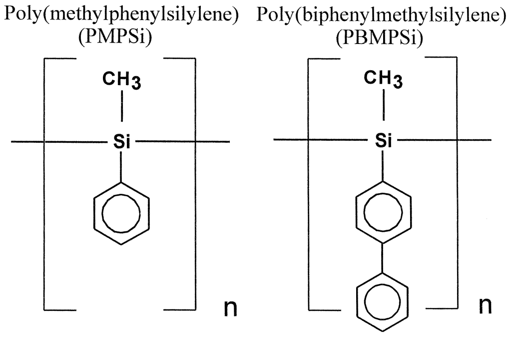

Scheme 1.

West [4]. The low-molecular weight fractions were extracted with boiling diethyl ether. The residual polymer, obtained in ca. 17% yield, possessed an unimodal but broad molecular mass distribution, $M_{\mathrm{w}} = 4.10^4$.

Thin films for photoconductivity measurements (thickness ranges from 2 to 4 μm) were prepared from a toluene solution by casting on conducting indium tin oxide or Au covered borosilicate glasses. The top semitransparent Al electrodes were prepared by vacuum evaporation. Before deposition the polymers were purified three times by precipitation in methanol and toluene solution and centrifuged (1200 rpm, 145 min). After deposition the films were dried at 10^{-3} Pa at 330 K for at least 4 h.

Infrared absorption spectra are given in Fig. 1. Tentative assignments for the vibrational bonds are based on the earlier assignments by Zhang and West [4] and completed by authors.

Fig. 2 gives data on ultra-violet visible (UV-VIS) absorption and luminescence spectra in solution and in the solid state. The exciton peak at 3.7 eV is a consequence of the $(\sigma$–$\sigma *)$ (bonding and antibonding molecular orbitals) absorption of all $(\mathrm{Si})_n$ segments in the amorphous and polycrystalline sample, the fluorescence maximum at 3.5 eV provides a better estimate for one-photon absorption of the longest segments. The ‘size’ of the excitation is ~ 25 bonds from the radiative power measurements [5]. The second exciton band with peak at about 4.4 eV occurs in the $(\pi$–$\pi *)$ transitions in the phenyl side groups.

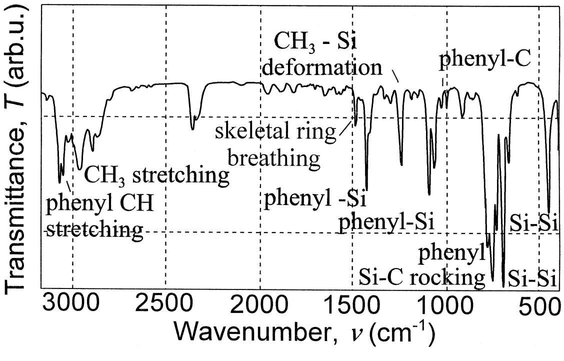

Fig. 1. Infrared spectra of PMPSi.

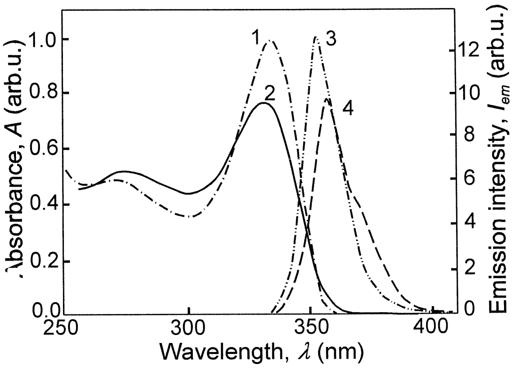

Fig. 2. Absorption spectra of PMPSi in tetrahydrofurane solution (curve 1: – · –) and in the solid state (curve 2: ————). Curves 3 (– · · –) and 4 (— —) represent luminescence spectra in tetrahydrofurane solution and in the solid state, respectively.

In the transient photoconductivity Nd–YAG laser with a dye laser and a doubler were used to produce a single shot ($\lambda = 330$ nm). Transient photocurrent was detected with low noise converter and digitizing oscilloscope. The vacuum temperature controlled cryostat was used both for the measurements and light-soaking experiments. A pulse modulated electron microscope ($U = 10$ kV and $I = 1$ nA) provided with the spectral electroluminescence apparatus was used for the electron induced metastability. For controlled light-soaking, both the water filtered Xe lamp (75 W) and Hg lamp (200 W) were used.

3. Results

The samples were irradiated by UV light around $\lambda_{\mathrm{inc}} = 350$ nm (using a bandpass filtered Xe lamp) and molecular weight of the polymer was measured

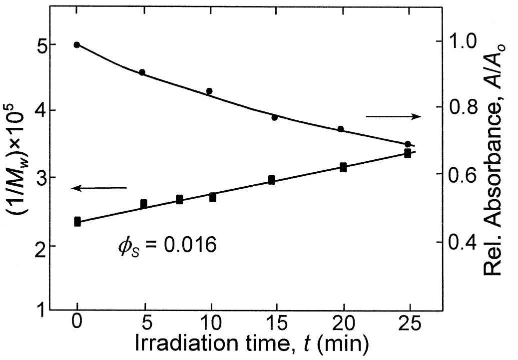

Fig. 3. Reciprocal value of the molecular weight of PMPSI vs. irradiation time ($\lambda = 350$ nm)(■). ϕ_s represents the quantum efficiency of polymer main chain scission. The lines are drawn as guides for the eyes.

by means of gel permeation chromatography. It is evident from Fig. 3 that the average molecular weight decreases with irradiation time. At the same time the shift of the position of the maxima of the absorption was observed (from 336 nm to 320 nm after 20 min irradiation). This shift supports the results concerning the Si–Si bond scission after UV irradiation.

From the flash photolysis measurements [6], it follows that the induced absorption consists of maximum at 360 nm and two broader smaller maxima at about 423 and 460 nm. The absorbance in the main maximum was determined as 0.009 cm^{-1}. The 360-nm absorption is assigned to the radical-cation (positive polaron) on the basis of the spectral data in the γ-irradiated rigid matrix at 77 K [7]. The smaller absorption at 460 nm is attributed to both silyl radical $\sim \text{SiR}_2$ and silylene biradical [8].

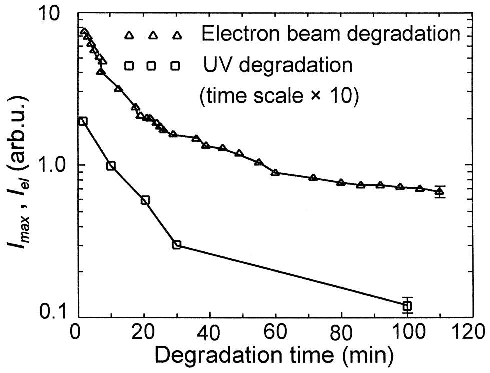

Fig. 4. The time evolution of the degradation both for the UV (Xe filtered, 75 W) radiation (□) and electron beam (10 kV, 1 nA) (△). The lines are drawn as guides for the eyes.

The time evolution of the degradation both for the UV (Xe) radiation and electron beam are in Fig. 4. It is necessary to point out that both plots differ in the output quantity—in the UV degradation experiments it was the amplitude of the TOF photocurrent signal and in the electron beam experiment it was an integral electroluminescence signal. The recovery of both signals after an anneal was, in both cases, at nearly original magnitudes.

4. Discussion

The main goal of the experiments was to determine the properties of the metastable states. For this purpose we used the post-transit spectroscopy described in Ref. [9]. The light soaking time evolution of the total collected charge, Q_{coll}, the dispersion coefficient, α, and the value of the photocurrent at the transit time, I_{max}, are depicted in Fig. 5. Also, the respective quantities after the anneal at $T_a = 370$ K for $t_a = 20$ min are given. It is obvious that all the quantities decrease with the light soaking, but the dependencies for Q_{coll} and α have a similar dependence compared to that of the photocurrent at the transit time I_{max}. Besides, both exhibit different annealing behavior as complete recovery of the photocurrent at the transit time I_{max} is achieved, whereas,

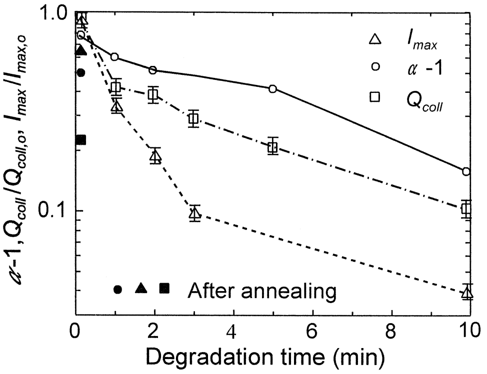

Fig. 5. The irradiation induced metastable states: time evolution the total collected charge Q_{coll} (□), the dispersion coefficient α (○) and the value of the photocurrent at the transit time I_{max} (△), also given are the values after anneal at 370 K for 10 min (■●▲). The lines are drawn as guides for the eye.

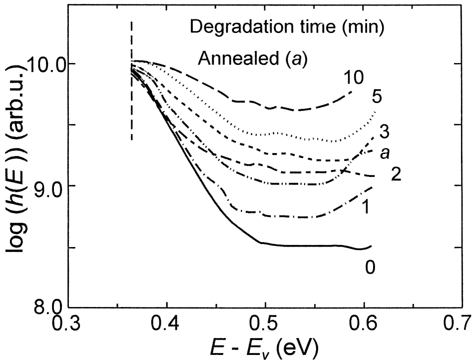

Fig. 6. The irradiation induced metastable states: time evolution of the metastable DOS function in the time interval $t \in (0,10)$ min, also given is the DOS after anneal at 370 K for 20 min (– · · –).

Q_{coll} and α after anneal do not reach the original magnitudes.

The irradiation induced metastable states expressed by the density of states (DOS) function are in Fig. 6. The evaluation and results are in accordance with our previous paper [10]. The progressive increases in DOS at the energy, 0.55 eV, with indication of some still deeper radiation generated states. The remarkable point is that those states after anneal at 370 K for 20 min do not anneal completely (see *a* curve in Fig. 6). The light-induced metastable states have been previously observed in transient photocurrent hole experiments by Naito et al. [11,12]. They interpret the metastable changes by creation of conformational changes in Si backbone. In Ref. [13], the authors calculated and observed photocreated metastable states in organopolysilane solids using light induced ESR. They found two types of light-induced centers, one for lower photo excitation (ca. 3.5 eV) due to the Si skeleton stretching forces and the other higher photo excitation (over 4.8 eV) creates weak bonds in several places of the Si skeleton.

5. Conclusions

The main conclusions are: (1) the observed phenomena are interpreted as the metastability in polysilylanes connected with the change of the conformation length that was correlated with the blue shift of the maximum energy of the absorption corresponding to σ–σ^* Si transitions; (2) the light soaking time evolution of the total collected charge, Q_{coll}, the dispersion coefficient, α, and the value of the photocurrent at the transit time, $I_{\max}$, causes decrease of all the quantities mentioned; (3) the temperature anneal $T_{\mathrm{a}} = 370$ K for $t_{\mathrm{a}} = 20$ min recovers the quantity $I_{\max}$, whereas only partial recovery of the quantities Q_{coll} and α is achieved.

Acknowledgements

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