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Visible Photo- and Electroluminescence of Poly[methyl(phenyl)silylene] Films

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1. Introduction

Polysilylenes, with their uninterrupted runs of silicon atoms, represent a new class of polymers with significant delocalization of electrons along the polymer chain. The high quantum efficiency of the photogeneration and the high charge carrier drift mobility of the order $10^{-8} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$, unusually high for polymeric photoconductors [1], stimulated the interest in the research. Recently, poly[methyl(phenyl)silylene] (PMPSi) was used as the hole transporting material in multilayer electroluminescent device [2]. Latter on, light emitted diodes (LED), utilizing PMPSi [3] and other polysilylenes [4] as active materials, were reported. PMPSi LED showed the electroluminescence (EL) spectrum which almost coincided with the photoluminescence (PL) spectrum, i.e. the main narrow peak was situated at 353 nm, whereas the maximum of the weaker broad peak was located at about 470 nm [3]. The origin of the visible emission was not fully clarified. The studies on model materials have suggested that branching may be responsible for the presence of visible photo- and electroluminescence [5,6]. In this paper we present new experimental results of EL, low-temperature PL, and thermostimulated luminescence (TSL) to obtain more information concerning the visible emission.

2. Experimental

PMPSi was prepared by sodium mediated Wurtz coupling polymerization. The low molecular fraction was extracted with boiling diethylether. The residual polymer possessed a unimodal but broad molar mass distribution, $M_w = 4 \times 10^4 \text{ g mol}^{-1}$. EL diodes consisted of an indium-tin-oxide (ITO)-coated quartz substrate, an emission layer of PMPSi and an indium-containing magnesium (In : Mg) electrode. The spin-coated polymer films ranged from 60 to 300 nm in thickness for EL, 500 nm for PL, and 1000 nm for TSL.

Current-voltage characteristics were measured using a power supply and electrometer. The emission intensity was detected by a photomultiplier (R 928, Hamamatsu Photonics Co.). PL spectra were measured in the range 4.2 - 300 K using SDL-1 and Hitachi MPF-4 spectrometer. Excitation was performed by light from either Hg or Xe lamp with appropriate filters or monochromator. TSL measurements were performed with an automatic equipment for optical thermoactivated spectroscopy over a temperature range from 4.2 to 350 K; uniform heating with the rate $\beta = 0.15 \text{ K/s}$ and fractional heating regime [7] was used.

3. Results

Figure 1 shows PL and EL spectra of PMPSi films 110 nm thick. The EL spectrum was nearly independent of the applied voltage and the film thickness. The peaks in the EL spectrum almost coincided with those in the PL spectrum (measured at room temperature). The sharp EL band, which is of excitonic feature connected with the polymer Si backbone, with its full width at half-maximum FWHM = 0.15 eV is narrower than that of PL (0.24 eV). The emission intensity increased monotonically with increasing injection current. The diodes with thicker polymer film exhibited stronger emission than those with thinner ones at the same current. It suggests the emission originates not only from the region near the interference between PMPSi film and Mg:In electrode, but also from the bulk of the film. Thus, not only the hole transport but also transport of electrons should be taken into account in PMPSi films.

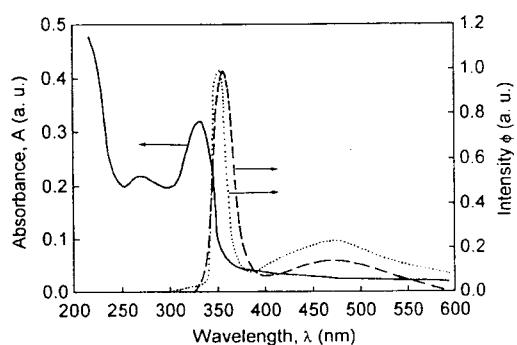


Fig. 1. Electroluminescence spectrum of ITO/PMPSi/In:Mg diode measured at 77 K (dotted line) and photoluminescence spectrum of PMPSi film measured at room temperature (dashed line). The photoluminescence was excited by 280 nm light; spectra are normalized by peak intensity.

PL spectra measured at different temperatures under excitation with $\lambda_{ex} = 313$ nm are shown in Fig. 2. At low temperatures the maximum of the broad visible PL is situated at about 410 nm (Fig. 2, curve 1), while at $T > 100$ K the maximum is shifted to about 500 nm (Fig. 2, curves 5 and 6). Excitation spectra monitored at 4.2 K for the sharp ($\lambda = 354$ nm) and broad ($\lambda = 410$ nm) emission contain both ($\sigma - \sigma^*$) ($\lambda \sim 345$ nm) and ($\pi - \pi^*$) ($\lambda \sim 265$ nm) optical transitions. The ratio of the peak intensities is different for both cases: the ($\sigma - \sigma^*$) transitions dominate in the case of the sharp peak, whereas for the broad band the ($\pi - \pi^*$) transitions prevail. In addition, an optical transition at 302 nm was found in the excitation spectrum of the broad visible emission (this transition was not found either in the excitation spectrum monitored by the PL sharp band or in the absorption spectrum). Interestingly, the position of this new band almost coincides with reported band with maximum at $\lambda = 302$ nm (4.1 eV) in the electroabsorbance spectrum [8].

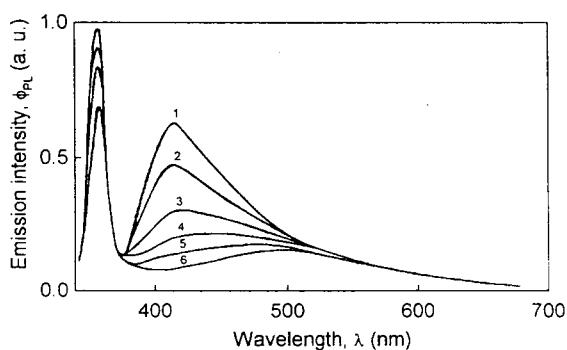


Fig. 2. Influence of temperature on photoluminescence spectra of PMPSi film. $T_{ex} = 4.2$ K (curve 1), 20 K (2), 30 K (3), 50 K (4), 100 K (5) and 150 K (6). Excitation light $\lambda_{ex} = 313$ nm.

TSL was found only in low-temperature region (peak at about 90 K). It indicates that only shallow localized states are present. The spectrum of TSL coincides with the broad visible PL. No short-wavelength

contribution was detected. Thus, the visible luminescence is, at least partly, connected with the recombination luminescence of localized charge carriers. Kinetics of the delayed isothermal recombination luminescence (ITRL), which was detectable for temperatures $T < 180$ K, is very long (10 s $> t > 2000$ s for $T = 5$ and 160 K, respectively). For all temperatures the decay could be described by a power function $I \sim A t^{-m}$.

Light-induced PL and TSL quenching was found for the first time. Figure 3a shows the effect of the reduction of the PL intensity after 30 min irradiation of the film with unfiltered UV light of 500 W Hg-lamp at 4.2 K (curve 2). The PL spectrum of the virgin sample is given as curve 1. With the prolongation of the irradiation time the PL intensity decreased (cf. Fig. 3b), but the PL spectrum profile remained unchanged. This effect showed a reversibility when the sample was heated to room temperature and after that cooled again for a further measurement run (Fig. 3a, curve 3). It was found that the complete reversibility of the PL intensity could even be achieved after 10 min UV illumination at 150 K (the illumination of the sample with unfiltered UV light at low temperature did not cause any optically detectable photodegradation; photodegradation products were only detected during the UV irradiation at room temperature). The process of the recover of the PL intensity showed clearly thermoactivated character; the temperature, at which the full recombination could be achieved was the same as that at which signal of the TSL disappeared.

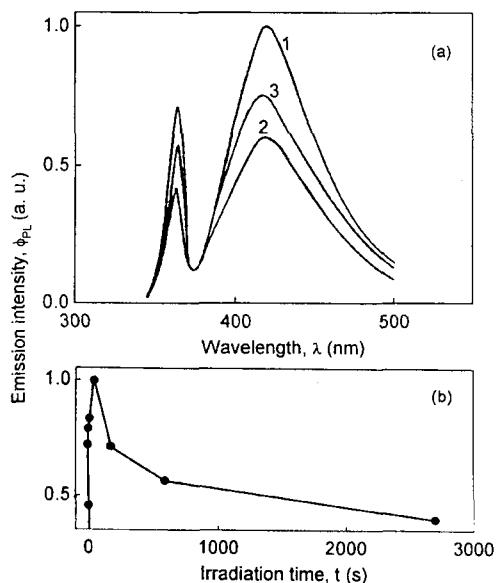


Fig. 3. (a) Photoluminescence spectra of cast PMPSi film; all detected at $T = 5$ K with $\lambda_{ex} = 313$ nm. Curve 1 - spectrum of virgin sample; curve 2 - spectrum after irradiation with unfiltered UV light at $T = 5$ K for 30 min; curve 3 - spectrum after annealing at $T_{ann} = 300$ K for 10 min. (b) Dependence of the total TSL intensity vs. irradiation time by UV unfiltered light at 4.2 K.

4. Discussion

It follows from Fig. 1 that the EL spectrum almost coincide with the PL one. The narrow UV band is of excitonic feature connected with the polymer Si backbone. The broad visible luminescence is still under consideration. Generally is taken into account that branching at Si backbone is responsible for visible PL and EL. From our measurements (cf. Fig. 2) of the temperature dependence of PL follows that the visible PL intensity strongly increases with decreasing temperature, so both exciton PL (EPL) and broad visible PL (BVPL) are of comparable peak intensity at 4.2 K. The shift of the position of BVPL maximum with temperature suggests that BVPL band is composed of several luminescent centres whose efficiency is

temperature dependent.

From the energy diagram it is evident that at least three energy levels are present in the gap: polaron level E_p , defect trap hole level (0.45 eV deep [7]) E_t^h , and level of charge-transfer exciton ${}^1(\sigma,\pi^*)^{\text{CT}}$. The last mentioned level could be partly responsible for the visible PL. The important property of BVPL is that it is more enhanced when the excitation is carried out by $(\pi-\pi^*)$ excitation of phenyl substituents as compared with the excitation by $(\sigma-\sigma^*)$ excitation of the silicon skeleton. This could be connected with the fast geminate recombination of charges generated during the $(\sigma-\sigma^*)$ excitation. The following photoinduced electron transfer to phenyl group forms the charge transfer exciton [9]. Spectroscopically speaking there is a direct radiationless deactivation process from the ${}^1(\pi,\pi^*)$ state to the ${}^1(\sigma,\pi^*)^{\text{CT}}$ state. According to the detail analysis of the fluorescence of arylsilanes and related compounds [9] it was stated that the intramolecular charge-transfer emission is located at about 400 nm. Because there is not preferable ground state geometry one can assume that this emission will be conformation dependent. Thus we can assume that short wavelength luminescence of BVPL at about 410 nm is connected with the emission from the ${}^1(\sigma,\pi^*)^{\text{CT}}$ CT state whereas the luminescence with the maximum at about 500 nm is connected with the branching of Si-Si skeleton.

5. Conclusion

The EL spectrum of the ITO/PMPSi/In:Mg diode was nearly independent of the applied voltage and of the film thickness. The peaks in the EL spectrum almost coincide with those in the PL spectrum. The narrow UV band is of excitonic feature connected with the polymer backbone. The broad visible band is connected with polymer branching, charge-transfer excitons with electrons localized on the phenyl ring and delocalized holes on the Si-backbone, and with the exciton-charge interaction and recombination.

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