電気材料技術雑誌 第10巻第2号
J. Soc. Elect. Mat. Eng. Vol. 10, No. 2, 2001


# Polarized Light Emitted Diodes Prepared on Light-modified Surface of Poly[methyl(phenyl)silylene]

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## 1. Introduction

Polarized light emitted diodes (LED) can be used in many electro-optical applications. Their fabrication needs an oriented surface for the deposition of an electroluminescent material. Traditional techniques of the rubbing of isotropic polymeric layers do not satisfy the increasing demands of the alignment quality. Therefore, the development of new, rubbingless technique has been of a great interest during last years. Some of new promising techniques are based on photosensitive polymers. In this paper we report the fabrication of polarized LEDs prepared on modified surface of poly[ethyl(phenyl)-silylene] (PMPSi) by light.

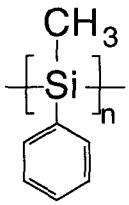
## 2. Experiment

PMPSi (see Fig. 1) was prepared by sodium mediated Wurtz coupling polymerization [1]. The low-molecular-weight fraction was extracted with boiling diethylether. The residual polymer possessed a unimodal but broad molar mass distribution, $M_w = 4\times10^4$ g $mol^{-1}$. Current-voltage characteristics were measured using a power supply and electrometer. The emission intensity was detected by a photomultiplier (R928, Hamamatsu Photonics Co.).

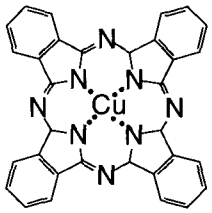
Poly[1,4-(2-(5-carboxypentyloxy)-5-methoxyphenylene)vinylene] (CPMOPPV) (see Fig.1) was prepared by dehydrochlorination polymerization of 6-(2,5-bis(chloromethyl)-4-methoxyphenyloxy)-hexanoic acid ethyl ester [2] with potassium tert-butoxide. 2-Methyl-2-propanol solution of potassium tert-butoxide was added dropwise to *p*-xylene and 2-methyl-2-propanol (1:1) solution of the monomer at room temperature under an inert atmosphere, and the mixture was refluxed for 24 h. The product was recovered by filtration, and resolved in water. Hydrochloric acid was added into the aqueous solution to obtain the orange precipitate of the final product [3].

Copper-phthalocyanine (CuPc) (see Fig. 1) was obtained from Tokyo Kasei and purified by sublimation.

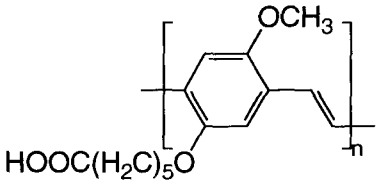
LED fabrication: Thin film of PMPSi was prepared from a chloroform solution by spin-coating technique (spinning speed 2000 rpm) on ITO glass substrate. Before deposition, the polymer was three times reprecipitated from toluene solution with




Poly[methyl(phenyl)silylene] (PMPSi)




Copper-phthalocyanine (CuPc)




Poly[1,4-(2-(5-carboxypentyloxy)-5-methoxyphenylene)vinylene] (CPMOPPV)

Fig. 1. Molecular structures of PMPSi , CuPc and CPMOPPV

methanol. The final toluene solution was centrifuged (12000 rpm, 15 min). After the deposition the film was dried at 0.1 Pa and 330 K for at least 4 hrs. Then, the PMPSi film was irradiated (120 min) by linearly polarized light using HBO 100 W mercury discharge lamp. After the irradiation a luminescent material was deposited, CuPc by vacuum evaporation ($10^{-4}$ Pa, 3 nm $s^{-1}$), CPMOPPV by spin coating (2400 rpm). In the latter case, after the deposition, the structure was dried at the same conditions as PMPSi. In the end, a top Al or Mg:In electrode was vacuum evaporated. The typical thickness were: PMPSi 110 nm, CuPc 50 nm, and CPMOPPV 80 nm.

## 3. Results

Fig. 2 shows photoluminescence (PL) and electroluminescence (EL) 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 associated 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 broad visible luminescence is associated with branching points in the polymer bulk. 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.

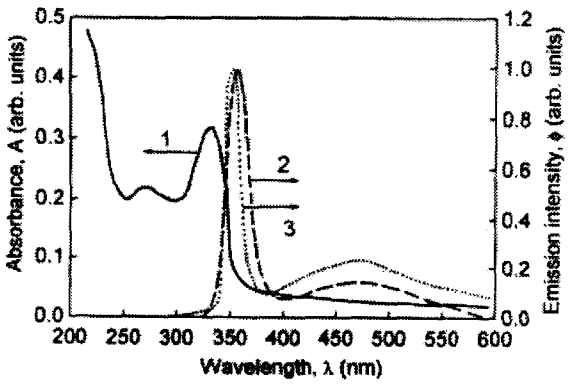



Fig. 2. Absorption spectrum of PMPSi film (curve 1), PL spectrum of PMPSi film measured at room temperature (curve 2), EL spectrum of ITO/PMPSi/In:Mg diode measured at 77 K (curve 3). PL was excited by 280 nm light; spectra are normalized by peak intensities.

Using the fact that the quantum efficiency of the electroluminescence of PMPSi films strongly depends on the length of the polymer chain, the photodegradation of PMPSi with linearly polarized UV light leads to the angular-dependent emission. The effect seems to be controlled by the angular-dependent photodegradation connected with formation of other photoproducts preferentially oriented along the light polarization [4]. Thus, the polarized LED can be fabricated. However, the emission quantum efficiency was very low. Therefore, another emission layer was applied.

On the PMPSi surface modified by light as mentioned above a low-molecular-weight or polymeric luminescent material (LM) with high emission efficiency was deposited. Thus, the structure: ITO/light modified PMPSi/LM/metal allowed us to fabricate an electroluminescent device emitting polarized light. Because PMPSi is a very good hole transporting material (charge carrier mobility is of order $10^{-8}$ $m^2$ $V^{-1}$ $S^{-1}$), the injection and transport of holes was not limited. The polar diagrams are given in Fig. 3. The emission ratio for two perpendicular polarizations was found as about 2 and 3 for CuPc (Fig. 3a) and CPMOPPV (Fig. 3b), respectively.

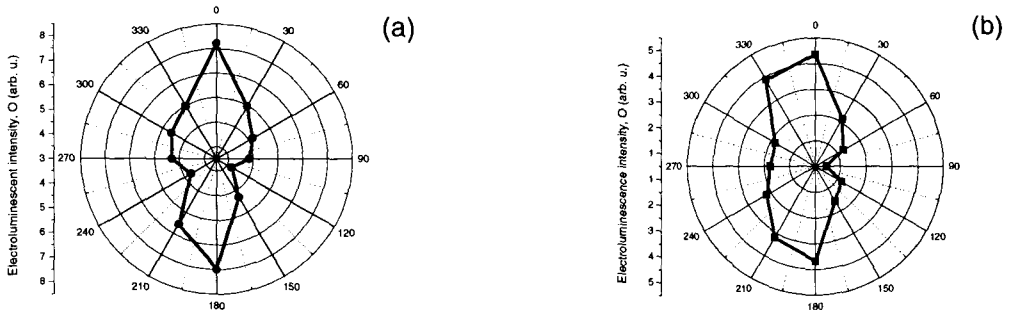



Fig. 3. Polar diagrams of the EL of the ITO/PMPSi/emission layer/Al cell. Emission layer: (a) CuPc, (b) CMPOPPV.

## 4. Discussion

Three photoprocesses in PMPSi are responsible for the alignment of the luminescent material: Si-Si bond scission, formation of polar ion-pairs, and photoablation of the surface. Thus, the mechanism of the photoalignment is associated with an anisotropic UV-light absorption by the conjugated Si-segments which result in photoinduced angular-dependent photoselection by the scission of the Si-Si chain and in formation of photoproducts, such as polysiloxane species and molecular dipoles formed by electron transfer from the Si main chain to the phenyl group with the following charge localization, preferentially within segments oriented along the light polarization. The fact, that a further change of primary director orientation can't be generated by the change of the electric field vector with respect to the initial sample orientation in a second irradiation procedure, can be interpreted in that way that the irreversible photochemical modification of the polymer chain is very probable.

**Acknowledgements**

The financial support by grants No. A1050901 from the Grant Agency of the Academy of Sciences of the Czech Republic, No. 202/01/0518 from the Grant Agency of the Czech Republic, and No. ME440 from the Ministry of Education, Youth and Sport of the Czech are gratefully appreciated.

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