Polarized Electroluminescence from Bilayer Structures

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Summary: The photoalignment ability of poly[methyl(phenyl)silylene] (PMPSi) films makes it possible to use them as hole-transporting substrates for the preparation of organic oriented films. A PMPSi layer prepared by spin coating was irradiated, after drying, with linearly polarized UV light. Then, water-soluble hydroxyaluminium phthalocyaninesulfonate [$Al(OH)Pc(SO_3Na)_{1-2}$] was deposited by casting. The cell ITO/PMPSi/$Al(OH)Pc(SO_3Na)_{1-2}$/Al showed non-linear current-voltage characteristics. For applied voltages higher than 10 V, polarized electroluminescence was observed. Its spectral characteristic consisted of two peaks with maxima at about 320 and 700 nm; their polarized anisotropies $R_{EL} = \Phi_{||} / \Phi_{\perp}$ were ca. 15 and 0.5, respectively.

Keywords: hydroxyaluminium phthalocyaninedisulfonate; photoalignment; polarized electroluminescence; poly[methyl(phenyl)silylene]

Introduction

Organic light emitting diodes (OLEDs), as one of the most promising candidates for the next generation of flat panel displays, have been extensively studied. Polarized OLEDs can be used in many electro-optical applications. Their fabrication needs an oriented surface for the deposition of an electroluminescent (EL) polymer or a special treatment (orientation) of the EL material. Several attempts have been made to prepare polarized OLEDs devices[1-4]. The development of new rubbing-less technique has been of great interest in the last years. Some of these techniques are based on photosensitive polymers. Their photoaligning ability is determined by the anisotropy of properties induced by light.

Poly[methyl(phenyl)silylene] (PMPSi) with significant electron delocalization along the chain[5]

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seems to be a suitable substrate material for the preparation of oriented organic films. If irradiated with linearly polarized light, it shows an angular-dependent photoinduced cleavage of Si-Si bonds, formation of polysiloxane structures, and quasi-stable photogenerated ion-pairs (dipoles), preferentially within segments oriented along the light polarization[6]. The organic material deposited in this way on the treated PMPSi surface is oriented[7]. Thus, we can simply prepare the ITO glass/hole-transporting PMPSi film/oriented EL material/ Al electrode cell, which can produce polarized electroluminescence. In this paper we report the fabrication of polarized OLEDs based on bilayer structure, consisting of PMPSi and a water-soluble phthalocyanine.

Experimental

Poly[methyl(phenyl)silylene] (PMPSi), $M_w = 4\times10^4$, was prepared by the Wurtz-coupling polymerization. The low-molecular-weight fraction was extracted with boiling diethyl ether. Hydroxyaluminium phthalocyaninesulfonate [$Al(OH)Pc(SO_3Na)_{1-2}$] sodium salt was synthesized by the following method. Hydroxyaluminium phthalocyanine was dissolved in 10 % fuming sulfuric acid and subsequently heated at 85 °C for 6 h. The reaction mixture was poured into a mixture of water and ice. The solid was filtered off, washed, dispersed in water and pH of the dispersion was adjusted with NaOH to ca. 11. Hydroxyaluminium phthalocyaninesulfonate changed into the dark, blue water-soluble sodium salt, which was isolated by evaporation of water on a water bath. The product, analyzed by HPLC, contained 47.3 % monosulfonated HOAlPC, 45.9 % disulfonated HOAlPc, 6.2 % trisulfonated HOAlPC and 0.7 % tetrasulfonated HOAlPc.

Thin (120 nm) PMPSi layers were prepared by spin-coating ITO glass with a toluene solution of PMPSi. Before deposition, PMPSi was centrifuged (12 000 rpm, 15 min). After deposition, the films were dried at 0.1 Pa and 330 K for at least 4 h. Then, the layer was irradiated with polarized UV light for 90 min using a mercury discharge lamp (HBO 100 W). A film of $Al(OH)Pc(SO_3Na)_2$ was deposited on the PMPSi layer by casting its water solution. The top Al electrode was vacuum-evaporated. Current-voltage (j~U) characteristics were measured using a Keithley 6175A electrometer. The emission intensity was measured with a photomultiplier system R928 (Hamamatsu Photonics Co.). The measurements were performed at room temperature. The polarized EL was measured using a polarizer placed between the sample and light detector.

Result and discussion

From the measurements of *j* ~ *U* characteristics of the ITO/PMPSi/Al cell (Figure 1) follows that current increases with increasing forward bias voltage, but the reverse bias current remains small; the cell exhibits rectifying characteristics. The emission intensity increases monotonically with increasing current injection. The electroluminescent efficiency was 3 × 10^{-5} %. The overall EL intensity of the photodegraded PMPSi film was about twice lower than that of the nondegraded film.

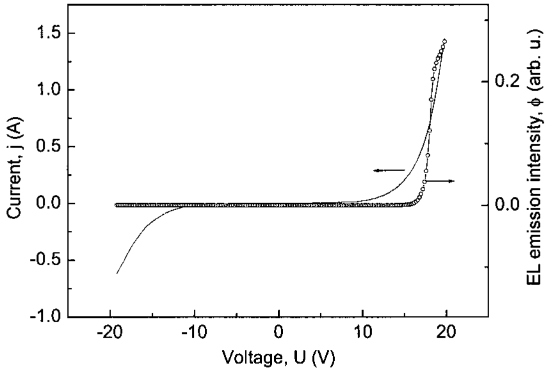

Figure 1. Current-voltage characteristics and dependence of EL emission intensity of the ITO/PMPSi/Al cell on applied voltage at room temperature, (PMPSi layer thickness 110 nm).

EL spectrum (Figure 2), measured at 77 K, nearly independent of the applied voltage, shows peaks at λ_{max} = 354 nm and λ_{max} = 470 nm; the peaks almost coincide with those in the photoluminescence spectrum. The sharp emission band, with its full width at half-maximum, FWHM = 0.15 eV, is narrower than that of the PL spectrum (0.24 eV). The narrow UV band is of excitonic nature associated with the polymer Si backbone.

The visible luminescence is related to the presence of branching points. The fluorescence quantum efficiency of PMPSi in solution was quite high, about 0.15 at 360 nm. The Stokes shift was ca. 19 nm in solution and ca. 26 nm in the solid state.

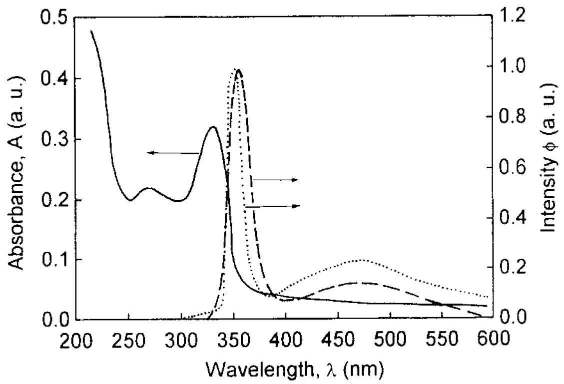

Figure 2. Absorption (solid line), photoluminescence (dashed line) and electroluminescence (dotted line) spectra of PMPSi film.

Irradiation of PMPSi with UV light (~ 350 nm) leads to Si-Si bond scission. The absorption at 340 nm (σ-σ^* transitions) decreases and the maximum is shifted to short wavelengths (Figure 3; degradation was induced by linearly polarized light from an HBO 100 W mercury discharge lamp).

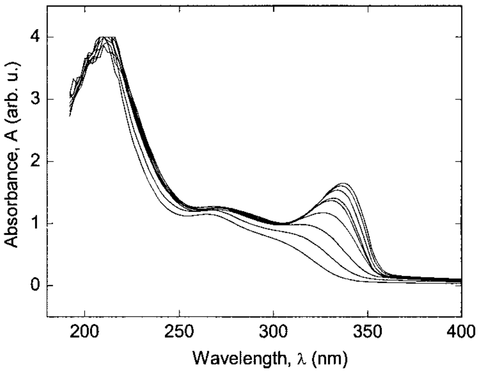

Figure 3. Absorption spectra of PMPSi film after UV photodegradation. The top curve is the spectrum of the non-degraded film; other curves are spectra of gradually photodegraded films (bottom curve – degradation 50 min).

Bond scission preferentially oriented along the light polarization resulted in anisotropic UV absorption and dichroism was also detected[7]. At the same time, polysiloxane structures were detected by IR spectroscopy, and cation radicals by flash photolysis[5]. In the presence of the cleaved Si-Si bonds, which form hole traps ca. 0.45 eV deep[8], quite a long life-time of ion-pairs was detected[9] (up to 2000 s at 160 K).

The anisotropic distribution of species, generated by angular-dependent photoselection, allowed for the preparation of oriented hydroxyaluminium phthalocyaninesulfonate layers. The feasibility of the preparation of oriented structures was preliminarily tested using liquid crystals; a twisted direction distribution was observed. The direction of the easy axis was parallel to the UV light polarization. The $j \sim U$ characteristics of the electroluminescent ITO/PMPSi (photodegraded)/$Al(OH)Pc(SO_3Na)_2/Al$ cell (Figure 4), shows a linear dependence for the applied voltages $U < 6.4$ V. For higher voltages, the current increases superlinearly. At $U = 10$ V, a strong increase in the current was observed with applied voltage. For the voltages $U > 11.5$ V, a trap-free current was observed ($j \sim U^2$) and polarized electroluminescence was detected.

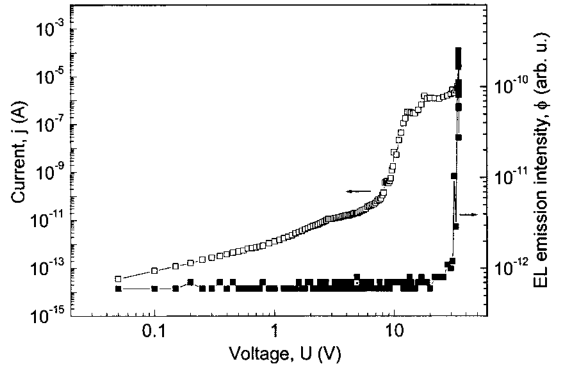

Figure 4. Current-voltage characteristic and electroluminescence emission intensity of the $ITO/PMPSi/AlOHPc(SO_3Na)_2/Al$ cell at room temperature.

Polarized EL spectra are given in Figure 5. The spectrum is typical of a phthalocyanine layer [10]. The spectral characteristic consists of two peaks with maxima at ca. 320 and 700 nm; their polarizing anisotropy $R_{EL} = \Phi_{||} / \Phi_{\perp}$ is about 15 and 0.5, respectively.

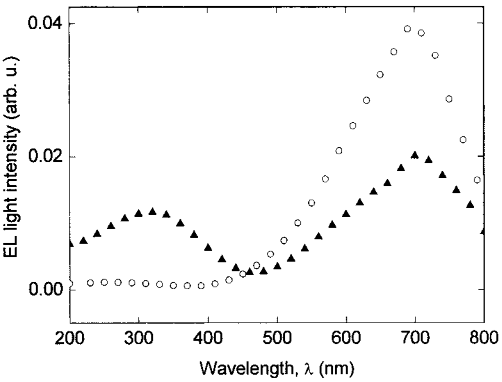

Figure 5. Polarized EL spectra measured at 80 V. The polarizing directions are parallel (solid triangle) or perpendicular (open circle) to the electric vector of the photoaligning light.

Conclusion

Polarized OLEDs of the ITO glass/photodegraded PMPSi/EL material/Al type can be prepared using PMPSi films treated with polarized light. The EL film deposited on the treated PMPSi surface shows an oriented structure, which produces polarized electroluminescence. It seems that the method can be generalized: EL films deposited on the treated PMPSi surface, both from solution and by vacuum evaporation, show polarized EL characteristics. Because PMPSi is a good charge-transporting material, the injection of holes into the diode is not limited.

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