

Light emission from the polythiophene derivative/ITO structure under electron beam excitation

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Abstract

Light emission of poly [3-(2-benzotriazolo) ethylthiophene] (PBET) at a different electron beam current density has been investigated by the cathodoluminescence (CL) spectroscopy. An electron beam was used to inject directly electrons and holes in the polymer. Under the low electron beam excitation the CL spectra show two peaks centered at 540 and 620 nm. Above some threshold beam current density, we observed an ultraviolet (UV) emission centered at 347 nm, in addition to the characteristic green–orange luminescence of PBET. The relative intensity of these bands was shown to depend on an electron beam current density and temperature. A ratio of the UV/green–orange band intensities increases with an increase of the current density and a decrease of temperature. The highest electron beam excitation used in our experiment at room temperature results in the UV-blue band broadening which is attributed to the charging effect and the structural change in the polythiophene derivative induced by the electron beam excitation. This effect could be used to obtain white light emission from the PBET/ITO structure.

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1. Introduction

Organic semiconductors have the potential to provide a compact, low-cost optical source-like light-emitting and laser diodes over a broad range of wavelength throughout the UV-visible spectrum. The large exciton binding energy in the conjugated polymers [1] and efficient excitonic recombination

can be the basis of high quantum yield devices operating at room temperature. Injecting electrons and holes into the charge states of the conjugated polymers leads to electroluminescence [2]. These carriers should be balanced at the junction of the emitting layer to yield the maximum exciton formation. Poly [3-(2-benzotriazolo) ethylthiophene] (PBET) used in this work was synthesized to increase quantum efficiency by introducing benzotriazole, an electron-withdrawing moiety, to the thiophene [3]. Singlet excitons are usually generated in polymer either by photoexcitation or by electrical injection of negative and positive charge carriers to the lowest unoccupied molecular orbital (LUMO) and the highest

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occupied molecular orbital (HOMO), respectively. Due to exciton binding energy and the lattice relaxation [4] the luminescence energy of polythiophene is usually lower than the HOMO–LUMO band gap, which is around 3.58 eV [5]. Both photoluminescence and electroluminescence spectra of the polymer show yellow–orange luminescence [6]. Studies of luminescence under high electron beam excitation are of interest in view of optically pumped lasing from the polymer and the prospects for electrically pumped laser. As high current density is a prerequisite for electrically stimulated lasing the effect of high electron beam excitation and nature of luminescent properties under electrically strained conditions are important.

In this paper cathodoluminescence of PBET has been investigated under various electron beam excitation conditions. An electron beam was used to inject directly electrons and holes in the polymer structure. Above some threshold beam current density, we observed an UV emission centered at 347 nm, in addition to the characteristic green–orange luminescence of PBET. The intensity of UV band increases relatively as the incident electron beam current density increases. This effect is more strongly pronounced at liquid nitrogen temperature. The room temperature electron beam irradiation with a large fluence at a high current density results in the broad blue luminescence and the saturation of the green–orange band intensity that could be interpreted as the structural change in the polythiophene derivate film under strong electron beam excitation.

2. Experimental

PBET was polymerized by the oxidation of ferric chloride as previously described [3]. A schematic experimental setup of the electron beam excitation of the device structure and the chemical structural formula of PBET is shown in Figs. 1(a) and (b). The 25 mm × 25 mm indium tin oxide (ITO) (13 Ω/square) glasses were etched prior to use as substrates. The emissive layer, consisting of PBET, was spin coated on the ITO substrate with a thickness of 200 nm. Polymer solutions for film preparation were made by dissolving a polymer of 40 mg into a tetrachloroethane of 1 ml. The films were dried to remove the solvent in a vacuum oven at room temperature. The samples were

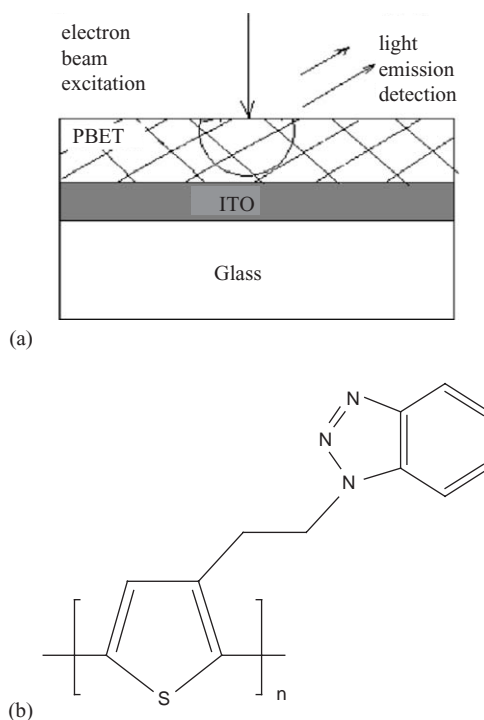


Fig. 1. (a) A schematic experimental setup of the electron beam excitation of the device structure. Poly (3-(2-benzotriazoloethoxy)thiophene (PBET) was spin-cast onto clean, indium tin oxide (ITO) glass substrate. (b) The chemical structural formula of PBET.

mounted on a stage of the field emission gun scanning electron microscope in a variable-temperature cryostat. Scans of an electron beam with the current densities in the range of 0.4 A/cm² to 2 kA/cm² for linetime of 0.2 ms through a 500 μm diameter aperture were used to inject electrons and holes in the polymer structure. The light emission detection and spectral measurements were made using a cathodoluminescence (CL) spectroscopy system. The light emitted from the sample is collected by a paraboloidal aluminum mirror and directed into the slits of the monochromator, which is mounted on the microscope. The accelerating voltage of electron beam for this study was 10 kV, which corresponds to a penetration depth of 0.2 μm as calculated from the Kanaya–Okayama model. The electron beam bombardment used in our experiment allows directly injecting electrons and holes with a high density in the polymer.

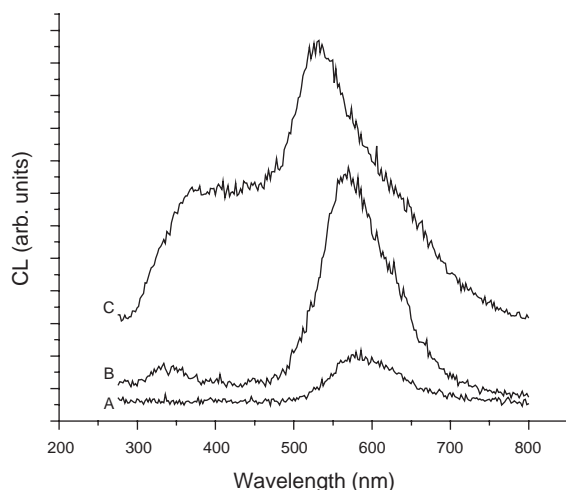


Fig. 2. CL spectra of PBET/ITO structure obtained at 10 kV accelerating voltage of incident electrons and at different electron beam current densities: (A) 0.4 A/cm², (B) 30 A/cm² and (C) 2 kA/cm².

3. Results and discussion

Room temperature CL spectra of the PBET/ITO structure under various electron beam excitations are shown in Fig. 2. Under the low-excitation conditions with an incident beam current density of 0.4 A/cm² the spectrum (Fig. 2, A) is similar to the photoluminescence spectrum previously reported [6]. The peak centered at 580 nm with a shoulder at 620 nm were attributed to the π - π^* transition of the conjugated thiophene segments. Under higher excitation with a beam current density of 30 A/cm² (Fig. 2, B) three peaks centered at 340, 565 and 620 nm are revealed. Under the highest excitation used in our experiment with a beam current density of 2 kA/cm² (Fig. 2, C) the broad ultraviolet-blue bands are detected. In addition, a blue shift of green luminescence in the spectrum up to 529 nm and a red shift of the UV peak to 370 nm are observed. The peak at 347 nm could be attributed to the direct interband radiative transition. The absorption spectrum of the PBET samples has a strong absorption band at 282 nm [6]. A relative intensity of the UV-blue band increases with increasing electron beam current density. It should be noted that the position of the 620 nm peak does not shift under the high beam current excitation.

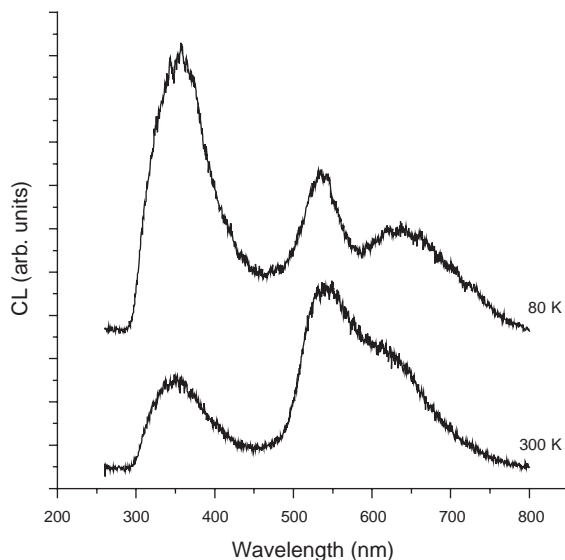


Fig. 3. CL spectra of the PBET/ITO structure acquired at 300 and 80 K at a 400 A/cm² electron beam current density.

Fig. 3 shows CL spectra of the PBET/ITO structure obtained under the high electron beam excitation at different temperatures. The UV band centered at 350 nm along with green–orange luminescence bands are clearly observed. The relative intensity of the bands depends strongly on temperature. At 80 K the polymer structure shows the high intensity of the UV luminescence, which is substantially higher than that of the green–orange luminescence. Some red shift of a 620 nm peak is also observed. Note that no shifts for the UV band and no blue band appearances are detected under such excitation conditions.

To investigate the origin of the blue band we measured the luminescence of the polymer structure after the electron beam irradiation with the high electron beam current density for various fluences and temperatures. CL spectra of the irradiated sample are shown in Fig. 4. As the fluence of the electron beam irradiation increases, the intensity of the broad violet–blue luminescence at 370–470 nm increases, while an intensity of the green–orange luminescence relatively decreases. The blue–violet band is detected under room temperature excitation, but it has not appeared under the highest electron beam current density excitation used at 80 K. The results indicate that the structural change in the polythiophene derivative may occur

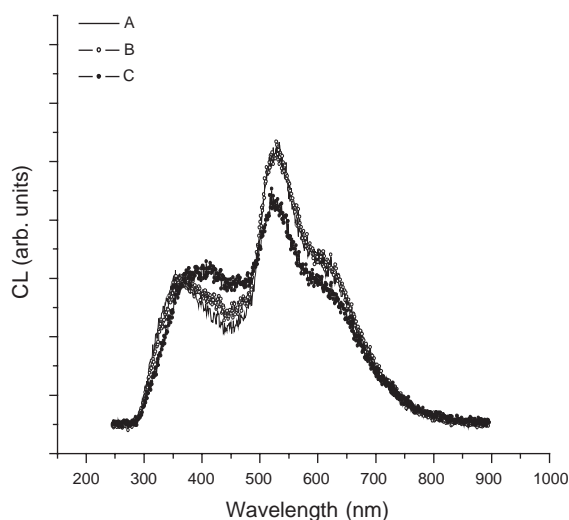


Fig. 4. CL spectra of the structure obtained after the electron beam irradiation at the 400 A/cm^2 electron beam current density for different fluences: (A) 1.5×10^{21} , (B) 3.0×10^{21} and (C) $5.5 \times 10^{21} \text{ cm}^{-2}$.

under the room temperature electron beam irradiation with a high fluence.

The most important observation is the appearance of additional UV and blue–violet emissions centered at 347 and 420 nm, respectively. The wide spectra with violet and UV emissions have been previously demonstrated in insulating polymers at high electric fields [7,8]. The high-energy photon emission in these systems was attributed to the so-called “impact ionization,” which occurs when the injected and thermally generated carriers are accelerated by a strong electric field to cause collision excitations and subsequent radiative recombination. Theoretical models [9] suggest that the number of these collisions increases with electric field, which can be arisen from the electron beam induced charging. Our experimental results indicate that an increase of the electron beam current density results in an increase of charging of the polymer and increasing of UV CL intensity. The charging effect in the polymer structure was clearly observed in a secondary electron mode and could be controlled by the electron beam current adjustment. The UV luminescence suggests to be associated with the recombination of “hot” nonequilibrium carriers in the presence of the strong charging effect. Impact excitation induced by the strong field due to electron beam charging of the

polymer produces a large number of excited carriers in excess of equilibrium (“hot” carriers). These excited states decay thus approaching their number at equilibrium via several competing mechanisms. Formation of singlet excitons, which decay radiatively emitting green luminescence, is one such possible mechanism. However, the strong charge effect inhibits this type of decay by dissociation of the excitons, thereby enhancing the direct HOMO–LUMO interband radiative transition with UV emission. Under such conditions direct radiative transition is favorable over exciton recombination. The saturation of the green luminescence at high current density is a further evidence for the partial inhibition of exciton recombination.

The appearance of the blue luminescence at high current densities is suggested by electron beam induced phase transformation in PBET at room temperature. When the polymer backbone conformations are coupled with that of the sidegroups the first-order phase transition is occasionally realized. Such polymers should show the bistable states, which are separated by a potential barrier in free energy. The phase conversion between the two states in some temperature region is thermally forbidden but may be possible by electron beam excitation. In the hysteretic temperature region of the phase transition the switching of the electronic phase was previously demonstrated by pulsed photoexcitation of electron-hole pairs in polythiophene [10]. The photoinduced change in the absorption and luminescence spectra arising from the structural change, which is generally termed photochromism, has been observed for many photochromic molecules with photoactive π -electron units and thin films of the semiconducting π -conjugated polymer [11]. The structural change induced by the photoexcitation is considered to be minimal with least steric hindrance but significantly affects the π -conjugation length or the electronic structure. The photoexcited electron-hole pairs or their lattice relaxed analogs (polarons) are responsible as precursors for the observed photoinduced phase transition. Origin of the blue luminescence from the films might be attributed to the electron beam induced change in the ring torsion angle by the interchain interaction in a substituted benzotriazole derivative segment. To understand clearly the electron beam induced spectroscopic changes, further studies should be carried out using additional techniques.

4. Conclusions

In summary, cathodoluminescence of the polythiophene derivative structure was investigated under various electron beam current excitations. UV and blue bands in the spectrum of the polymer structure at the high electron beam current density are observed. The band intensities increase as an electron beam current density increases while the green–orange luminescence is saturated. The charge effects of the polymer suggest to inhibit the green luminescence by dissociation of the excitons, thereby enhancing the direct interband radiative transition with UV emission. The room temperature electron beam irradiation with a large fluence at a high current density results in the broad blue luminescence that may be attributed to the structural change in the polythiophene derivative film under strong electron beam excitation. The effects of the electron beam induced spectroscopic change of the polymer could be used to obtain white light luminescence from the polythiophene derivative structure.

Acknowledgements

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