Vol 16 No 5, May 2007
1009-1963/2007/16(05)/1464-03
Chinese Physics
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and IOP Publishing Ltd

Transient demonstration of exciton behaviours in solid state cathodoluminescence under different driving voltage*

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(Received 11 September 2006; revised manuscript received 6 November 2006)

In the solid state cathodoluminescence (SSCL), organic materials were excited by hot electrons accelerated in silicon oxide (SiO_2) layer under alternating current (AC). In this paper exciton behaviours were analysed by using transient spectra under different driving voltages. The threshold voltages of SSCL and exciton ionization were obtained from the transient spectra. The recombination radiation occurred when the driving voltage went beyond the threshold voltage of exciton ionization. From the transient spectrum of two kinds of luminescence (exciton emission and recombination radiation), it was demonstrated that recombination radiation should benefit from the exciton ionization.

Keywords: electroluminescence, ionization
PACC: 7860F, 3280D

1. Introduction

Understanding of the mechanisms underlying exciton decay, including the effect of high electric field, is an outstanding challenge in organic optoelectronic devices. The most used examples are photovoltaic phenomena,[1] electroluminescence (EL)[2−7] and thin film field effect transistors.[8,9] The exciton ionization occurs on the expense of the electron affinity of the acceptor molecule, it largely compensates the attractive Coulomb interaction of the separated holes (h) and electrons (e).[10] Now we focused on transient exciton behaviours in solid state cathodoluminescence (SSCL). No matter what the excitation is electric or optic, the electron and hole are bounded and formed exciton by Coulomb interaction due to the low dielectric constant of organic materials. In general, the binding energy of Frenkel exciton is more than 0.1eV and the radius of exciton is smaller than 1nm. For MEH-PPV, the binding energy of exciton is about 0.7(±0.15) eV.[11] Practically there is hair-like difference between photoluminescence and EL spectra due to exciton emission without and with an applied electric field. The SSCL was firstly discovered by our research group and intensively studied in terms of experimental and theoretical efforts.[12−14] The characteristic spectra of SSCL are the appearance of two emission peaks: one is exciton emission and the other is recombination radiation due to the ionization of exciton. The generality of SSCL has been examined in many organic materials, such as PPV,[13] MEH-PPV[15] and Alq_3.[16] In the report, we would like to further confirm our latest experimental result published in Ref.[12] by the study of the transient spectra.

2. Experiment

Indium Tin Oxide (ITO) coated glass substrates with a sheet resistance of 60 Ω/□ were cleaned consecutively in ultrasonic baths containing ethanol, acetone and DI-water. The first SiO_2 thin film was prepared by electron beam evaporation at the growth rate of 0.5Å/s under the high vacuum of $2.66\times^{-4}$ Pa. Poly[(2-methoxy-5-(2′-ethyl-hexyloxy) phenylene vinylene] (MEH-PPV) was dissolved in

*Project supported by the National Natural Science Foundation of China (Grant Nos 10374001, 10434030 and 60576016), State Key Development Program for Basic Research of China (Grant No 2003CB314707), the Excellent Doctor's Science and Technology Innovation Foundation of Beijing Jiaotong University of China (48011).
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chloroform with a concentration of 5mg/ml. The MEH-PPV thin film was fabricated on the top of the first SiO_2 layer by spin-coating method. The second SiO_2 layer was prepared under the same condition as the first layer. The top Al (ca. 100nm) electrode was prepared by thermal evaporation. The EL spectra were measured by SPEX Fluorolog-3 spectrometer. The time behaviours of EL were measured by Tektronix TDS 540D four-channel digital phosphor oscilloscope.

3. Results and discussion

Based on the ITO/SiO_2/MEH-PPV/SiO_2/Al device driven by sinusoidal voltage, SSCL was obtained. The SSCL spectra of MEH-PPV are shown in Fig.1 under different driving voltages. SSCL characteristic spectra are the emergence of shorter wavelength when the driving voltage goes beyond a certain voltage according to the thickness of each layer. The spectra consist of two emission peaks, the emission peak at 585nm is the exciton emission of MEH-PPV which obeys molecular theory,[15] the emission peak at 403nm is recombination radiation which benefits from the ionization of MEH-PPV exciton and obeys band model.[12] In this paper, we will intensively discuss the relationship between exciton emission and recombination radiation by transient spectrum. Here, we also notice blue shift of exciton emission from 585 nm to 572 nm with the increase of driving voltage. The small blue shift of exciton emission peak may be attributed to the polarization of MEH-PPV exciton with the increase of driving voltage.

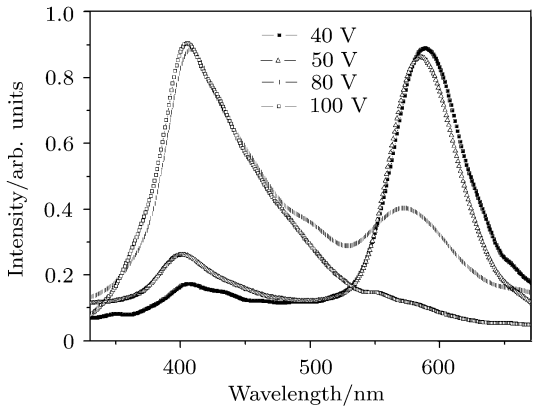


Fig.1. EL spectra of MEH-PPV under different driving voltage.

When the luminescence sign obtained by photoelectric multiplied diode and the applied sinusoidal electric sign were connected with the Tektronix TDS 540D four-channel digital phosphor oscilloscope. The time behaviours of luminescence dependence on the value of driving voltage were measured. When we monitored the emission peak at 585nm, the relationship between luminescence intensity and driving voltage was measured and is shown in Fig.2. Solid lines were intended for visualization of relationship between emission intensity and driving voltage. MEH-PPV exciton emission intensity (585nm) firstly increases with the increase of driving voltage and then decreases with the increase of driving voltage. The decrease of exciton emission intensity with the increase of driving voltage should be attributed to the exciton ionization. In order to clarify exciton emission intensity dependence on the value of driving voltage, we expressed the process of exciton emission by the following rate equations. The rate of exciton formation is

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = \sigma_2 n G^* [G + \sigma(E) n_2] - \frac{1}{\tau} n_2 - \sigma(E) n_2. \quad (1)$$

And the intensity of exciton emission is

$$B_2 = \frac{1}{\tau} n_2. \quad (2)$$

The intensity of recombination radiation due to exciton ionization is

$$B_1 = \sigma_1 n [G + \sigma(E) n_2], \quad (3)$$

σ_1 is the probability of recombination radiations, σ_2 is the probability of excitons formation, n is concentration of hole at t time, $G^* = G$ is the total concentration of electron, n_2 is the concentration of excitons, $\sigma(E)$ is the probability of exciton ionization in an electric field strength E and τ is the lifetime of exciton.

Because the probability of exciton ionization (σ) is strongly determined by applied electric field strength (E).[17] According to the Eqs.(2) and (3), the intensity of exciton emission should decrease when the driving voltage goes beyond the threshold voltage of excitons ionization. To deeply understand the exciton emission process of SSCL, the exciton emission transient intensity dependence on the driving voltage is studied. There are three characteristic driving voltages; the first $V(t_1)$ is the threshold voltage of SSCL. The ratio of exciton formation is larger than that of exciton ionization when the driving voltage ranges from $V(t_1)$ to $V(t_2)$. The ratio of exciton formation is less than that of exciton ionization when the driving voltage ranges from $V(t_2)$ to $V(t_3)$.

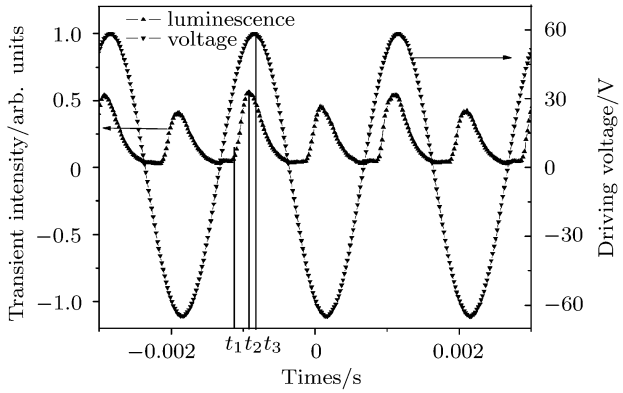


Fig.2. Exciton emission (585 nm) brightness–voltage waveform at 60 V 500 Hz.

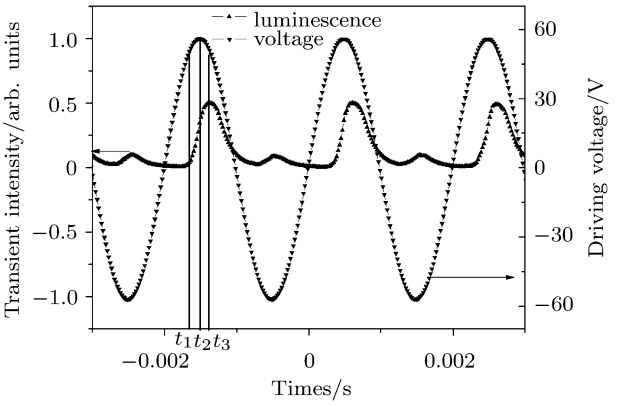


Fig.3. Recombination radiation (403 nm) brightness–voltage waveform at 60 V 500 Hz.

When we monitored the emission peak at 403nm, the relationship between luminescence intensity and driving voltage was obtained and is shown in Fig.3. The emission peak at 403nm is recombination radiation due to exciton ionization. Although excitons are ionized, the electrons and holes are still confined in MEH-PPV thin film sandwiched by SiO_2. The sole route of electron returned to ground state is combination radiation. Why does the intensity of 403nm arriving to the maximum value lag the voltage arriving to maximum value? We must notice the threshold voltage of exciton ionization. From Fig.3, we can know that $V(t_1) = V(t_3)$ is the threshold voltage of exciton ionization. The ratio of exciton ionization is larger than that of exciton formation when the driving voltage is larger than $V(t_1) = V(t_3)$. So the intensity of recombination radiation arrives to the maximum value at t_3 time.

4. Conclusion

The polarization of exciton has been observed from SSCL under different driving voltages. The exciton emission peak shifts to shorter wavelength due to exciton polarization. As for the SSCL, recombination radiation intensity increases with the increase of driving voltage. Although excitons are ionized by the applied electric field, the electron and hole are still confined in MEH-PPV thin film sandwiched by SiO_2 and give recombination radiation. The behaviours of exciton are related to the applied electric field strength. Excitons are polarized under low applied electric field and are ionized under high applied electric field. If the free electrons and holes (generated by exciton ionization) are confined in organic materials, they will give recombination radiation. If not, luminescence will be quenched.

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