

Mixed excitation mechanism in solid-state cathodoluminescence structure

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Abstract

Mixed excitation was observed based on solid-state cathodoluminescence (SSCL) structures under alternating-current (AC) applied voltages, and it combines charge carrier injection recombination and hot electron impact excitation. Under AC voltages of 500 Hz, the electroluminescence from an ITO/SiO_x/MEH-PPV/SiO_x/Al device contained two emission bands: a blue emission band peak at 3.02 eV (410 nm) and an orange emission band peak at 2.10 eV (590 nm). The source of these two emission bands was investigated. Our experimental results suggest that the orange emission comes from the recombination of MEH-PPV excitons, and the blue emission is from oxygen defects and interface states of SiO_x.

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1. Introduction

For alternating-current thin film electroluminescence (ACTFEL) devices, achievement of blue emission for commercial application is a bottleneck problem. Suitable host materials with a wide bandgap and excellent carrier transport ability have not been found yet, and the brightness and efficiency are still unsatisfactory. For organic light-emitting diodes (OLEDs), the crucial and additional disadvantages for their potential application are lifetime and efficiency problem. Due to the possibility of combining the luminescence properties of organic semiconductor polymers with the stability of inorganic semiconductors, the study of hybrid organic–inorganic systems is very significant.

Solid-state cathodoluminescence (SSCL) is a new mechanism of light emission in organic–inorganic systems [1–3]. Compared with traditional cathodoluminescence ray tubes (CRTs), the process of electron acceleration for SSCL occurs in inorganic semiconduc-

tors rather than in vacuum. Here, it is worthy to mention that the excitation mechanism for the hot electron is similar to that of high-energy photons to excite emission of photoluminescence (PL); in this way the limitation of the spin statistic rule is broken, and triplet excitons that have no contribution to emission can efficiently be avoided, so the spin statistic rule (i.e., excitons are formed in the ratio of one singlet to three triplets) invalidates in SSCL. Moreover, high-energy electrons remain in excited states instead of going down to the ground state after impact excitation, and then recombine with an injected hole to emit light like traditional injection electroluminescence (EL). In theory, a high luminescent efficiency could be achieved by utilizing the integration of impact excitation and injection recombination in SSCL.

In our previous Letter, we confirmed that the energy of hot electrons accelerated by SiO_x thin films can reach up to 10 eV [4], which is enough for impact excitation polymer moleculars to form excitons. In this Letter, we obtained two emission bands, peaks at 3.02 eV (410 nm) and 2.10 eV (590 nm), by utilizing MEH-PPV as an emissive layer with the symmetrically configured

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SSCL structure with ITO/SiO_x/MEH-PPV/SiO_x/Al, under AC bias. The excitation mechanism for these two emissions bands had been investigated.

2. Experimental details

The SSCL device with MEH-PPV as an emissive layer was prepared as shown in Fig. 1. The first SiO_x layer was deposited on glass slides precoated with indium–tin–oxide (ITO, sheet resistance 80 Ω/□) by electron beam evaporation (EVA450, Alliance Concept Co. Ltd., France). During the deposition process, the base pressure in the chamber was kept less than 10^{−6} Torr, and the glass substrate temperature was kept at 200 °C. MEH-PPV (5 mg/ml dissolved in chloroform) was spin coated on the first SiO_x layer. The thickness of the MEH-PPV layer was about 40 nm. Subsequently, the second SiO_x layer was deposited on the MEH-PPV layer at 150 °C. The deposition rate of both the SiO_x layers was kept at 1 Å/s, and the growth thickness of the SiO_x layer, which was monitored by a quartz crystal microbalance mounted within a deposition chamber, was 100 nm. The thickness of the MEH-PPV layer was measured by a step apparatus (XP-2, AmBios Technology). The top electrode Al was prepared by thermal evaporation with a thickness of about 200 nm. The devices were operated under a sinusoidal voltage with 500 Hz. The photoluminescence (PL) spectra and electroluminescence (EL) spectra were measured by a Spex Fluorolig-3 spectrophotometer. The brightness voltage curves obtained were mapped by an oscillograph (Tektronix TDS 540D; four-channel digital phosphor Oscilloscope). All of the measurements were performed at room temperature under ambient pressure conditions.

3. Results and discussion

The EL spectra of SSCL with a 40 nm MEH-PPV driven by AC voltages of 500 Hz are shown in Fig. 2. The emission band has two peaks at 3.02 eV (410 nm) and 2.10 eV (590 nm), respectively. From Fig. 2a, we can see that the relative intensity of the blue light is increased with applied voltages from 40 to 75 V but that of the orange light diminished gradually. When applied

Al cathode
SiO _x (100 nm)
MEH-PPV
SiO _x (100 nm)
ITO

Fig. 1. The schematic diagram of the SSCL structure.

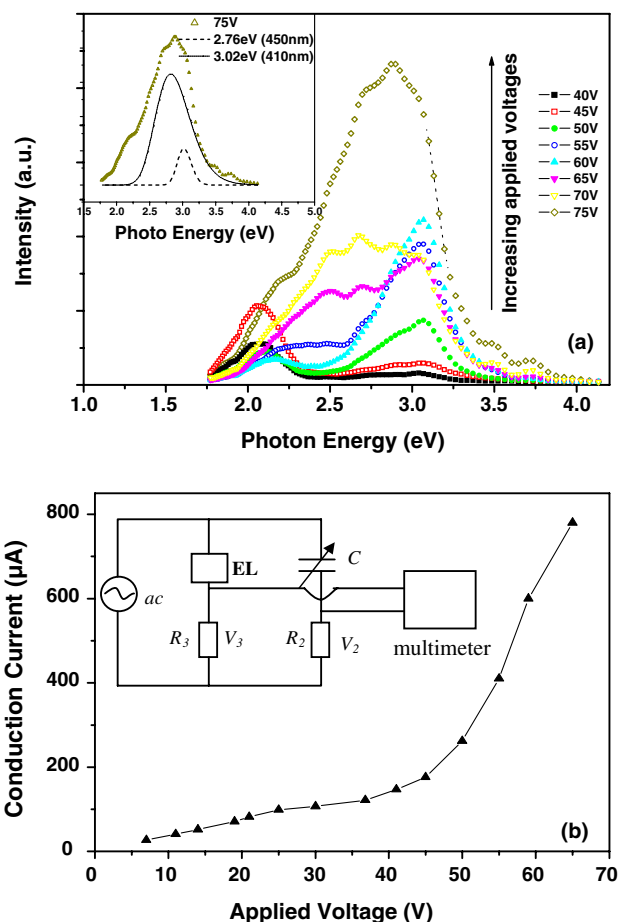


Fig. 2. (a) EL spectra from ITO/SiO_x/MEH-PPV (40 nm)/SiO_x/Al at different voltages: dotted line, 3.02 eV (410 nm) subpeak; dashed line, 2.76 eV (450 nm) subpeak. (b) Conduction current vs. applied voltages. Inset: bridge circuit used to measure conduction current; the resistance, $R_1 = R_2 = 1 \text{ K}\Omega$, is used. Under the luminescence threshold voltage, the capacitance C is adjusted to make the electric bridge balance, that is, $\Delta V = V_1 - V_2 = 0$. Above the threshold voltage, the device begins to light up, then, $\Delta V = V_1 - V_2 = 0$, and the conduction current is $I = \Delta V/R_1$.

voltages reached 60 V, the orange emission vanished completely and a broad spectral band, ranging from 3.10 eV (400 nm) to 2.48 eV (500 nm), appeared subsequently. This broad band blue-shifted with and increasing applied voltage, and was decomposed into two subpeaks at 3.02 eV (410 nm) and 2.76 eV (450 nm) (see the inset in Fig. 2a). We believe that the orange light originates from the recombination of MEH-PPV excitons as reported in the literature [5]. But the origin of the blue emission is interesting; the conduction current of SSCL was measured by a bridge circuit shown in Fig. 2b. Above 40 V, the conduction current abruptly increased with applied voltages, meanwhile, the orange emission appeared.

In order to investigate the origin of the blue emission, we further fabricated the ITO/SiO_x (200 nm)/Al single-layer device. The EL spectrum of the device ITO/SiO_x (200 nm)/Al device has the only emission initially

located at 2.76 eV (450 nm) [6]. This blue emission shifted to 3.02 eV (410 nm) with increasing applied voltages (as shown in Fig. 3). Hence, we can deduce that blue emission originated from the SiO_x layer. Zhuge et al. [7] confirmed that this emission came from neutral oxygen defects (NODs). So the two short-wavelength subpeak emissions of SSCL were attributed to the NODs in the SiO_x layer.

In addition, the characteristics of the brightness voltage of the SSCL were measured as shown in Fig. 4a and b. From this, we can see that there is almost no orange emission on inverse voltages in the ITO/MEH-PPV (40 nm)/Al device, which is in contrast to the almost similar emission intensity of the orange emission at both forward and inverse voltages in SSCL devices (ITO electrode connected with the positive pole). The orange emission has a leading phase angle relative to applied voltages in SSCL devices that is the so-called ‘leading edge emission’ [8]. This implies that the emission mechanism of the orange light in these two devices is completely different. Compared with injection electroluminescence in ITO/MEH-PPV/Al devices, orange emission in SSCL devices is the result of hot electron impact excitation. Blue emission was not observed on inverse voltages (as shown in Fig. 4c). Moreover, blue emission is in phase with applied voltages. So it implies that the main emission mechanism of blue light is injection electroluminescence [9]. The difference between both excitation mechanisms can be explained as follows: although the potential barriers have some effect on luminance for hot electron impact, the acceleration ability of the host material is the dominant factor to its luminance. Therefore, there is no obvious difference between forward and inverse voltages in the case of the hot electron impact mechanism. In injection EL, however, potential barriers are the dominant factors which affect luminance. So the carrier injection and luminance intensity are different when the device is driven by forward or inverse voltages.

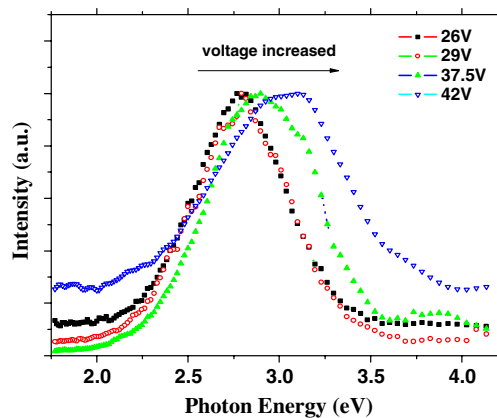


Fig. 3. EL spectra of the ITO/ SiO_x (200 nm)/Al device under different alternative current (AC) voltages.

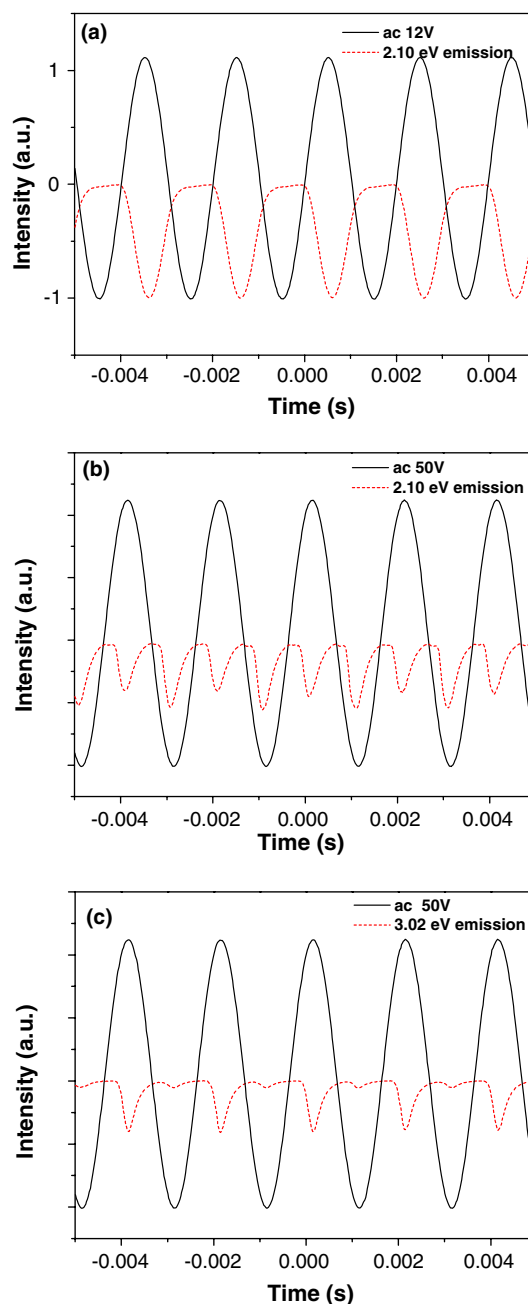


Fig. 4. Brightness oscillograms: 2.10 eV (590 nm) emission in the ITO/MEH-PPV/Al devices (a); 2.10 eV (590 nm) (b) and 3.02 eV (410 nm) (c) emission peaks in SSCL devices. Solid line: applied voltage; dotted line: brightness.

In order to confirm the emission mechanism of these two peaks, we studied a variety of intensity ratios of the two peaks at different the applied voltages and frequencies (see Fig. 5a and b). Initially, the orange emission intensity increased with applied voltage, and then decreased with further increasing the applied voltage. The reason is that the number of hot electrons accelerated by SiO_x layers increased with applied voltages; therefore the intensity of the orange emission is enhanced. On further increasing the applied voltage,

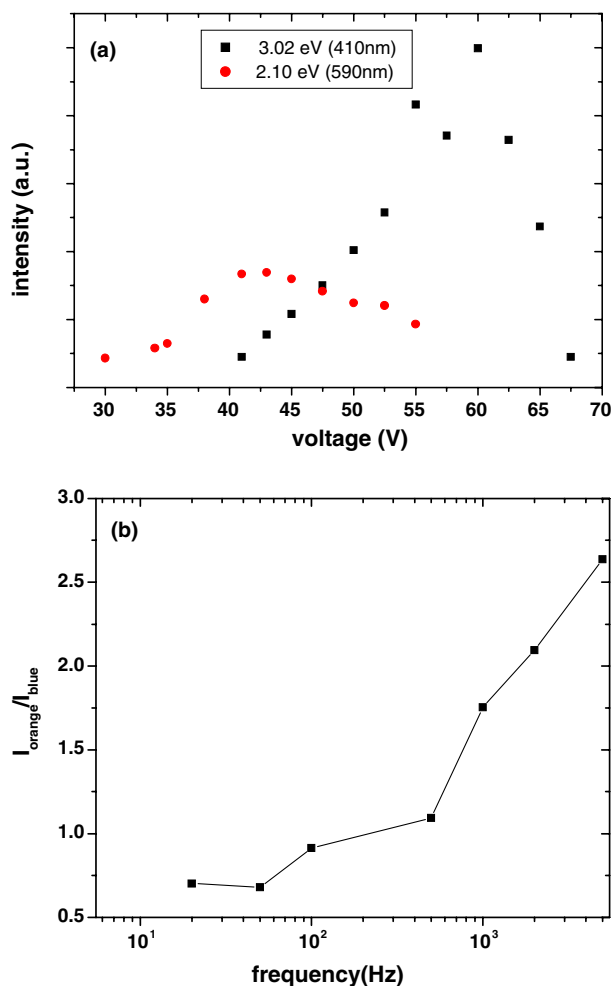


Fig. 5. The characteristics of the intensity ratio of the two peaks at different applied voltages (a) and at different frequencies of 50 V (b).

on the other hand, MEH–PPV excitons could disassociate in high fields; hence the intensity of the orange emission decreased. The trend of blue emission intensity increasing with applied voltage is due to the increment of ionized excitons. The intensity ratio of the orange emission to blue emission increased with applied voltage frequency, the reason being that the emission mechanism of the orange emission involves hot electron impact but that of blue emission is carrier injection. By increasing the applied voltage frequency, the impact period of the hot electrons increased; therefore the orange emission increased. However, space charges accumulated at the interface decrease with increasing frequencies; the injected carriers decreased and consequentially the blue emission intensity decreased.

Therefore, the emission mechanism of SSCLs can be explained as follows: hot electrons accelerated by the

SiO_x layer impact MEH–PPV to form excitons for irradiative recombination and remain in excited states and recombine with holes injected from the opposite electrode via interface states or impurity sites to produce blue emission. With increasing applied voltages, the MEH–PPV excitons disassociate in high fields, so the orange light diminishes gradually. The carriers produced by exciton disassociation reach luminescent centers in the SiO_x layer; hence the intensity of blue light increases.

4. Conclusions

In summary, we have fabricated SSCL devices using MEH–PPV as an emissive layer. Driven under AC voltages, the origin of the two emission bands has been investigated in detail. The orange emission comes from the recombination of MEH–PPV excitons impacted by hot electrons accelerated in the SiO_2 layer, and blue emission originates from oxygen defects and interface states of silica.

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