

1.54 μm electroluminescence from ErQ doped ADN organic light-emitting diodes

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Abstract: A near-infrared (NIR) organic light-emitting devices (OLEDs) was demonstrated with emissive layers (EMLs) based on erbium (III) tris(8-hydroxyquinoline) (ErQ) and the blue host material of 9,10-di-beta-naphthylanthracene (ADN). The fundamental structure of the devices is (p-Si/NPB/EML/Bphen/Bphen:Cs₂CO₃/Sm/Au), where three sets of EMLs (ErQ/ADN bilayer, (ErQ/ADN) \times 3 multilayer, and ErQ:ADN doped layer) have been compared. In all the three structures, 1.54 μm electroluminescence was observed due to the $4I_{13/2} \sim 4I_{15/2}$ transitions of Er³⁺. Compared with the ADN/ErQ bilayer structure, the NIR electroluminescence (EL) intensity is stronger by three times in the ADN:ErQ(1:1) doped structure. The ADN:ErQ composite films with different doping levels were further characterized by the measurements of absorption, photoluminescence and photoluminescence decay time. The results indicate effective energy transfer from ADN host to emissive molecular ErQ in the NIR EL process.

Key words: near-infrared; organic light-emitting device; erbium (III) tris(8-hydroxyquinoline)

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有机发光二极管中 ADN 掺杂 ErQ 的 1.54 μm 电致发光

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摘要: 自行设计了基于 8-羟基喹啉铈(ErQ)为发射层(EMLs)和二硝酰胺铵(ADN)为蓝光主体材料的近红外有机发光二极管. 器件的基本结构为(p-Si/NPB/EML/Bphen/Bphen:Cs₂CO₃/Sm/Au), 设计并比较了三套不同发射层结构(ErQ/ADN为双层结构器件,(ErQ/ADN) \times 3为多层结构器件,ErQ:ADN为掺杂结构器件)的器件. 三组器件在一定的偏压下,均可发出 1.54 μm 的光,对应三价铈离子 $4I_{13/2} \rightarrow 4I_{15/2}$ 的跃迁. 其中,ADN:ErQ(1:1)掺杂结构的近红外电致发光强度是 ADN/ErQ 双层结构中的三倍. 此外,不同掺杂浓度的 ADN:ErQ 复合膜做了以下表征:吸收谱、光致发光谱和荧光寿命谱. 实验结果证实了在近红外电致发光过程中存在从 ADN 主体分子到 ErQ 发射分子的高效率的能量转移.

关键词: 近红外发光;有机发光二极管;8-羟基喹啉铈

中图分类号: O433.1, O472+.3 **文献标识码:** A

Introduction

Recently, near-infrared (NIR) electroluminescence (EL) from Si-based organic light-emitting devices (OLEDs) has been intensively investigated because of their potential applications in optical communication, planar optical amplifiers, NIR illumination and

bio-imaging^[1-2], where the 1.54 μm emission is particularly attractive for its good agreement with the spectral window for the long-haul optical communication systems and for silicon photonics^[3]. Since Gillin reported Si-based OLEDs using erbium (III) tris(8-hydroxyquinoline) (ErQ) as emissive layers^[4], many efforts have been made to obtain 1.54 μm EL, where Er³⁺ + com-

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plexes have been frequently used for the 1.54 μm OLEDs^[5]. However, EL of Er complex still behaves weak, because Er^{3+} is difficult to be excited. Therefore, selecting a proper host organic material with efficient energy transfer to Er^{3+} is quite demanding to efficiently excite Er^{3+} and then enhance the NIR emission.

In a previous study, we have fabricated Si-based OLEDs using Tris (dibenzoylmethane) mono (phenanthroline) erbium (III) ($\text{Er}(\text{DBM})_3\text{phen}$) as dopant, 4,7-diphenyl-1,10-phenanthroline (Bphen) as host and electron transport layer to realize the Er^{3+} EL^[6]. In this report, we use ErQ as the dopant and 9,10-di-beta-naphthylanthraene (ADN) as the host material in order to enhance the Er^{3+} excitation and then its EL. ADN is an efficient blue host material, and its EL spectrum covers a wavelength range of 410 to 510 nm^[7]. There is a considerable overlap between the photoluminescence spectrum of ADN and the absorption spectrum of ErQ. The EL efficiency is markedly improved with a suitable ADN: ErQ doping level.

1 Experiment

The anodes and substrates were p-type (100) oriented silicon wafers with a resistivity of $\sim 10 \Omega \cdot \text{cm}$. After routinely cleaned, the silicon wafers were etched for 2 min in a 2% HF solution to remove the native oxide layer. Then the 2-nm SiO_2 layers on the front sides of the silicon substrates were grown in the oxidation furnace at 400 $^\circ\text{C}$ for 40 min to improve the resulting device performance by the passivation of the silicon surface states and the control of the hole injection. Al layer with a thickness of 60 nm was deposited by thermal evaporation on their backsides and annealed at 500 $^\circ\text{C}$ for 10 min in pure N_2 atmosphere for ohmic contact. The silicon wafers were transferred into an evaporation chamber with a base pressure of 5×10^{-6} Torr. A 130 nm-thick stacked organic layer was then deposited, comprising of a hole transport layer N,N'-bis-(1-naphthyl)-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB), a light-emitting layer ADN: ErQ, an electron

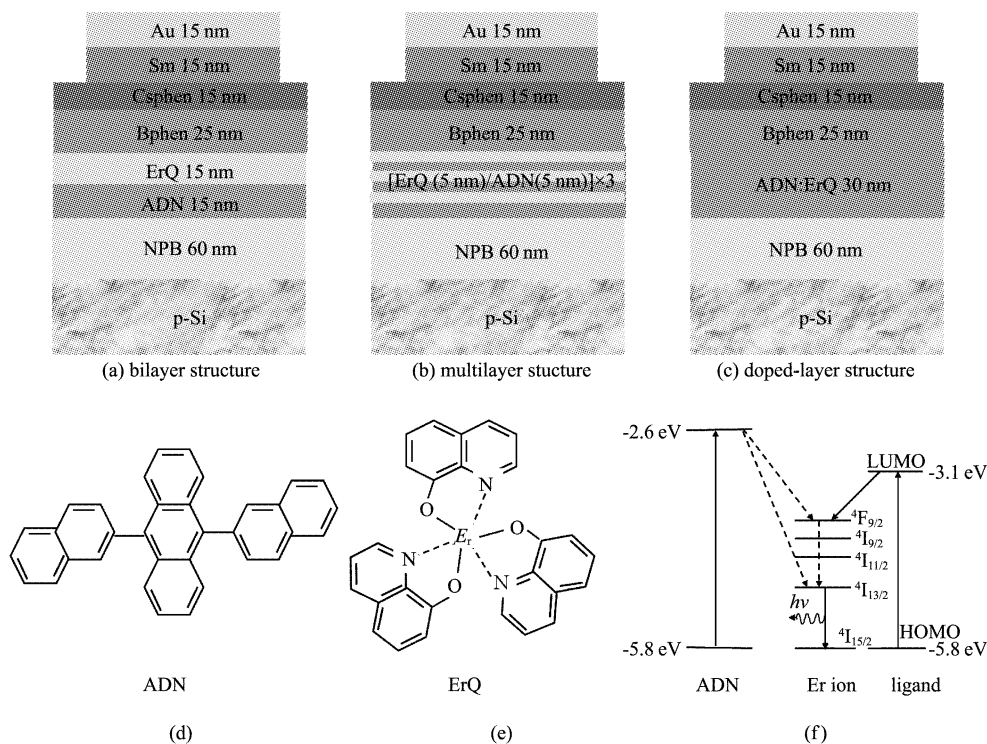


Fig. 1 The schematic structures of (a) the bilayer structure, (b) multilayer structure, and (c) doped-layer structure. Molecular structures of (d) 9,10-di-beta-naphthylanthraene (ADN) and (e) erbium (III) tris(8-hydroxyquinoline) (ErQ). (f) Energy level diagram of ADN and ErQ, and energy transfer processes in electroluminescence

图1 (a)双层器件结构示意图,(b)多层器件结构示意图,(c)掺杂器件结构示意图,(d) 8-羟基喹啉铒(ErQ)的分子式和(e)二硝酰胺铒(ADN)的分子式,(f) ADN和ErQ的能级图和电致发光中的能量传递过程

transport layer Bphen, and the electron injection layer Bphen:Cs₂CO₃ (mass ratio of 1:1, short for Csphen). Upon Csphen layer, Sm and Au layers were deposited through a shadow mark with circular holes 3 mm in diameter as a semitransparent cathode. The deposition rates of metals and organic materials were 1-2 $\text{\AA}\text{s}^{-1}$, monitored by a quartz oscillator. The resulting OLED has a structure of p-Si / NPB 60 nm/ ADN: ErQ 30 nm/ Bphen 25 nm/ Csphen 15 nm/ Sm 15 nm/ Au 15 nm. The device was designed by referring to the previous study^[6]. As shown in Fig. 1, we refer to the OLED with ADN (15 nm)/ ErQ (15 nm) emissive layers as the bilayer structure, that with [ADN (5 nm)/ ErQ (5 nm)] \times 3 layers as the multilayer structure and that with ADN: ErQ (1:1) (30 nm) layer as the doped-layer structure.

When measuring the NIR EL, the devices were driven by square pulses with a frequency of 11 Hz and a duty cycle of 1:1, and measured by a liquid-nitrogen cooled Ge detector. The absorption of ErQ thin film was examined using a UV-Vis spectrophotometer (Lambda 35). All measurements were carried out in air at room temperature.

2 Results and discussion

The typical top-emission EL spectra for the three sets of Si-based OLED are shown in Fig. 2. The typical 1.54 μm peak is the characteristic emission of Er³⁺ ions from the transition $4I_{13/2} \sim 4I_{15/2}$. At the same voltage of 4.0 V, and the nearly same current of 48, 44 and 43 mA, respectively, the EL intensity in doped structure is near three times and 1.5 times higher at 1.54 μm than that in the bilayer and the multilayer structure, respectively.

In all the ErQ-ADN structures, there are three possible 1.54 μm emission processes. (1) Injected electrons and holes form excitons in the host molecules ADN, and the excitonic energy is transferred to the nearby central metal Er³⁺ ions for 1.54 μm light emission^[8]. (2) ErQ absorbs the photons from ADN, and emits 1.54 μm light. (3) Injected electrons and holes form excitons in ErQ and the excitonic energy is transferred to the central Er³⁺ ions to emit 1.54 μm light. In the theory of the Forster type energy transfer^[9], the

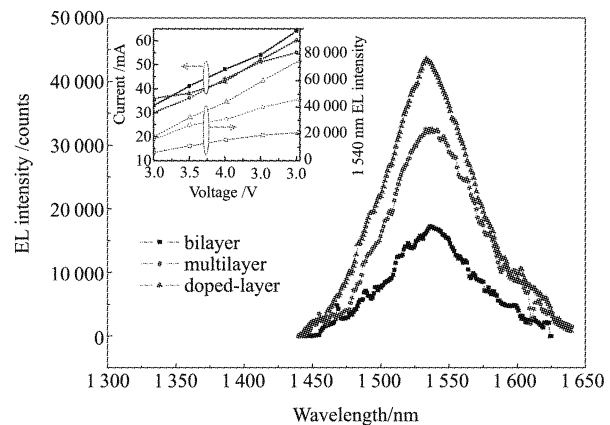


Fig. 2 EL spectra measured at the voltage of 4.0 V for the bilayer structure, multilayer structure and the doped layer structure. The inset shows their I-V curves and the EL intensity at the peak wavelength of 1 540 nm in a typical operation range of 3 ~ 5 V

图 2 在 4V 电压下测的三种器件的电致发光光谱, 插图为在典型操作电压 3 ~ 5 V 下的 I-V 曲线和 1 540 nm 发光波长下的电致发光强度

probability of the energy transfer is directly proportional to the overlap area between the emission spectrum of the donor and the absorption spectrum of the acceptor. In Fig. 3, there exists a considerable overlap between the photoluminescence spectrum of ADN and the absorption spectrum of ErQ. Moreover, the photoluminescence lifetimes of the ADN in different structures change largely, as shown in Table 1. It is 6.89 ns for the pure ADN structure. For the doped layer (1:1) structure, it is 3.83 ns, much smaller than that for the pure ADN structure. This indicates that ErQ quenches the excitons in ADN as represented in process (1). The results prove that the doped structure has a more remarkable 1.54 μm emission due to process (1).

Table 1 Photoluminescence life times of three different structures 表 1 三种不同结构器件的荧光寿命

Devices	PL life time	
	τ_1 (ns)	τ_2 (ns)
Pure ADN structure	6.89	47.79
Doped-layer structure	3.83	41.65
Multilayer-layer structure	4.16	41.00
Bilayer structure	6.43	47.28

In order to obtain more efficient 1.54 μm EL, we have optimized the ratio of doping level of ADN to ErQ. In Fig. 4 (a), the device with ratio of 1:1 do-

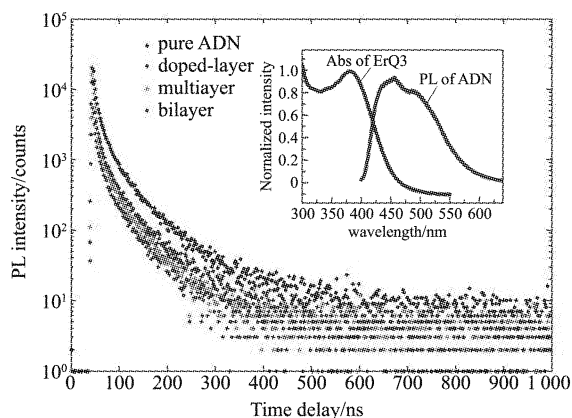
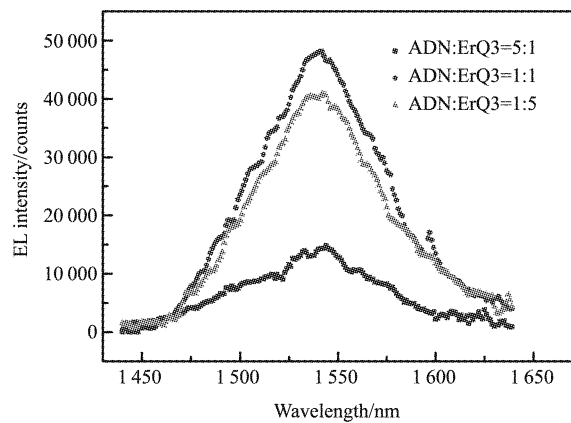


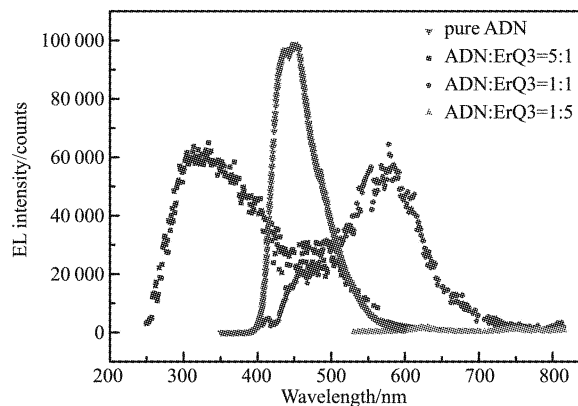
Fig. 3 Photoluminescence lifetime spectra for the ADN structure, doped-layer structure, multilayer structure, and bilayer structure. The inset shows the photoluminescence spectrum of ADN and the absorption spectrum of ErQ
图3 ADN器件、掺杂器件、多层和双层器件的荧光寿命谱,插图为ADN的光致发光光谱和ErQ的吸收谱

ping level has the highest $1.54 \mu\text{m}$ EL intensity, nearly 4 times larger than that of 5:1 doping level and 25% more than that of 1:5 doping level. In the device of 5:1 doping level, there are not enough Er ions to receive energy transferred from the excitons formed in ADN, and in the device of 1:5 doping level, Er ions are sufficient but the excitons in ADN are not. The device of 1:1 doping level may have the matched quantities of ADN and ErQ molecules at this energy transfer rate, which also indicates that the energy transfer from ADN to Er^{3+} is more efficient than that from the ErQ ligand to the central Er^{3+} ions.

Fig. 4 (b) shows the visible EL spectra of the three structures and the photoluminescence spectrum of the single-layer ADN. The peak wavelength of ADN is about 460 nm, the devices with 1:1 and 5:1 doping levels are 580 and 330 nm, respectively. Red-shift in the emission of device with 1:1 doping level is caused by the ADN-Bphen exciplexes^[10]. Charges transfer from the electron emitting layer host (donor) to the electron transmitting layer (acceptor) to form a charge transfer complex (exciplex) at the interface between the electron emitting layer host and the electron transport layer because of the large energy difference of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels. The formation of an exciplex also leads to a



(a)



(b)

Fig. 4 (a) NIR EL spectra measured at the voltage of 4.0 V for the doped layer structure with the ADN:ErQ doped ratio 1:1, 5:1 and 1:5. (b) Visible EL spectra of 5:1 structure, the 1:1 structure, the 1:5 structure and the pure ADN structure

图4 (a)在4 V电压下测量的ADN:ErQ不同掺杂浓度(1:1、5:1和1:5)的近红外电致发光光谱(b)不同掺杂浓度器件和纯ADN器件的可见光部分的电致发光光谱

broadened spectrum relative to the emissions of the individual acceptor or donor. Comparing with ADN film, the EL emission peak of ADN:Bphen film shows red shift from 460 to 580 nm. The energy level corresponds to the difference between the LUMO level of Bphen and the HOMO level of ADN, proving that ADN and Bphen molecules form the exciplexes upon excitation. In addition, the red-shifted emission peaks disappear in the EL spectrum of the device with 5:1 doping level and the pure ADN device, indicating that few excitons form the exciplexes. There is blue-shifted emission with the peak wavelength of 330 nm in the EL spectrum of the device with 5:1 doping level. We have not clear explanation for that now.

As the ADN content decreases, the visible EL intensity decreases largely. Compared with the 5:1 device, the visible EL intensity for the 1:1 device decreases by 60 times and that for the 1:5 device is too weak to be detected and is referred as the background line. The fact that ErQ reduces the visible EL of the ADN indicates that the energy transfer from ADN to ErQ occurs.

3 Conclusion

We demonstrated the 1.54 μm EL from Si-OLEDs with the ErQ/ADN bilayer, (ErQ/ADN) \times 3 multilayer, and ErQ: ADN doped layer with varying doping levels, among which the 1:1 doped structure is the most efficient one in 1.54 μm EL. High-efficiency intersystem energy transfer between Er complex and ADN is responsible for the efficient 1.54 μm EL.

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