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Influence of the electric characteristics of II–VI semiconductor material on the electroluminescence of lanthanide complex

F.-J. Zhang[1,a], Z. Xu[1,b], Y.-G. Lv[2,3], J.-C. Zhang[2], S.L. Zhao[1], J.-Z. Huang[1], Y. Wang[1], G.-C. Yuan[1], D.-W. Zhao[1], and X.-R. Xu[1]

[1] Institute of Optoelectronic Technology, Key Laboratory of Luminescence and Optical Information, Beijing Jiaotong University, Beijing 100044, P.R. China
[2] Institute of Modern Catalysis, State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China
[3] Chemistry-Pharmacy College of Jiamusi University, Jiamusi 154007, P.R. China

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Abstract. The organic-inorganic combined structural device (ITO/PVK:Eu/ZnS/Al) is fabricated based on layered optimization scheme. II–VI semiconductor material ZnS is acted as an electron function (transporting and acceleration) layer. The hot electrons which have been accelerated in the ZnS layer directly impact excitation europium ions through resonant energy transfer and then recombine with injected holes to form excitons in PVK or EuTTA$_2$(N-HPA)Phen. Europium (Eu) ions may also be excited by intramolecular energy transfer from ligands. There are two kinds of excitation mechanisms: impacted excitation and injected recombination for the combined structural device. The electroluminescence (EL) intensity of the combined structural device is strongly improved and reaches up to 381 cd/m^2 at 20 V compared with the pure organic structural device. It may be an effective method to improve the EL intensity of the lanthanide complex by using electric characteristics of inorganic semiconductor materials.

PACS. 79.20.La Photon- and electron-stimulated desorption – 73.50.-h Electronic transport phenomena in thin films – 72.20.Jv Charge carriers: generation, recombination, lifetime, and trapping

1 Introduction

Electric characteristics of inorganic II–VI semiconductor ZnS have been intensively studied by theoretical effort via Monte Carlo Simulation and experimental demonstration [1]. The injected electrons are accelerated by the ZnS layer and become hot electrons. The energy of hot electrons can reach up to 6 eV. This is high enough to impact excited luminescent materials [1]. A new kind of field induced luminescence was discovered when organic material is sandwiched by SiO$_2$ or ZnS under alternating current (AC) excitation [2–4]. In this case, the electrons are accelerated in solids instead of accelerating them in vacuum. We must take into account the limitation effect of the conduction band structure and choose a definite material. Cubic ZnS is a good candidate material as an electron transporting and acceleration material. The inorganic EL intensity is increased by using semiconductor materials, for example SiO$_2$, ZnS, as electron acceleration layer in the layered optimization scheme [5–8]. Emission from inorganic materials can not be detected in the traditional scheme, but it is clearly observed in the layered optimization scheme.

Throughout the last decade, the interest in electroluminescence of lanthanide (Ln) complexes was increased due to their attractive properties, such as long lifetime, large Stokes shift and line-like emission. However, since their f–f transition is inhibited due to spatial distribution of charge, they absorb very little excited energy [9–11]. So Ln(III) ions are chelated with ligands that have broad and intense absorption bands. The ligand absorbs energy or captures an electron-hole pair and then transfers it to the lanthanide ions. In the paper, we report that there are two routes for the excitation of lanthanide ions based on the organic-inorganic combined structural device: (i) hot electrons directly impact excitation the lanthanide ions through resonant energy transfer; (ii) ligand absorbs energy or captures an electron-hole pair and then transfers itself energy to the lanthanides ions through intramolecular energy transfer. The combined structural device may be an effective way to improve the EL intensity of Lanthanide ions.

2 Experiments

The EuCl$_3$·6H$_2$0 + TTA:N:H(2:1) 1:3:1Phen (EuTTA$_2$(N-HPA)Phen) was synthesized by Dr. Lv. The chemical

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[a] e-mail: `zhang_fj@tom.com`
[b] e-mail: `zhengxu@center.njtu.edu.cn`

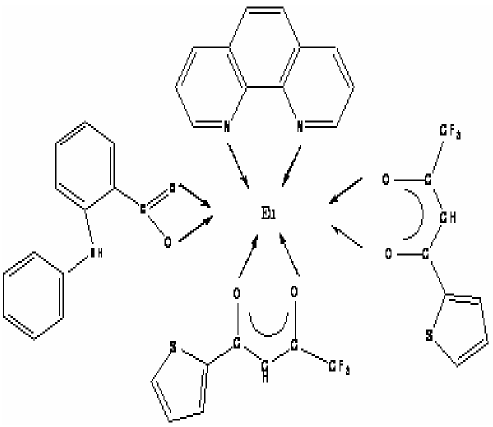

Fig. 1. Chemical structure of $EuTTA_2$(N-HPA)Phen.

structure of $EuTTA_2$(N-HPA)Phen is shown in Figure 1. Here, poly (N-vinylcarbazole) PVK was dissolved in chloroform with concentration 10 mg/ml. In order to improve the performance of $EuTTA_2$(N-HPA)Phen thin film, $EuTTA_2$(N-HPA)Phen was doped into PVK at weight ratio of 1:3. Indium Tin Oxide (ITO) coated glass substrates with a sheet resistance of 60 ohm/Sq. were cleaned consecutively in ultrasonic baths containing acetone, ethanol and DI-water. The PVK: $EuTTA_2$(N-HPA)Phen thin film was fabricated on the top of cleaned ITO coated glass substrate by spin-coating method. 2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline (BCP) and aluminum quinoline (Alq_3) films were fabricated by thermal evaporation at a rate of about 0.3 Å/s under high vacuum of 2×10^{-6} Torr. ZnS thin film was prepared by Electron Beam Evaporation at the growth rate of 0.5 Å/S under high vacuum of 2×10^{-6} Torr. The top Al electrode was prepared by thermal evaporation about 100 nm. The active emission area is about 2.25 π mm^2. The EL spectra were measured by SPEX Fluorolog-3 spectrometer at room temperature. The luminance was measured by PR-650 spectra-scan spectrometer. The current–voltage characteristics of the devices were analyzed using a Keithley Source Meter 2410.

3 Results and discussion

Two kinds of structural devices were fabricated and signed a symbol A and B, respectively.

Device A: ITO/PVK: $EuTTA_2$(N-HPA)Phen
(60 nm)/ZnS(80 nm)/Al.
Device B: ITO/PVK: $EuTTA_2$(N-HPA)Phen
(60 nm)/BCP(10 nm)/Alq_3(8nm)/Al.

As we all know, BCP thin film is acted as a hole blocking layer and Alq_3 thin film is acted as an electron transporting layer for the device B. In the device A, semiconductor ZnS thin film is acted as electron funct ion (transporting, acceleration) layer and hole blocking layer according to its electric characteristics and energy level instead of BCP and Alq_3 thin films in the device B. The energy levels diagrams of these two kinds of devices are shown in Figure 2.

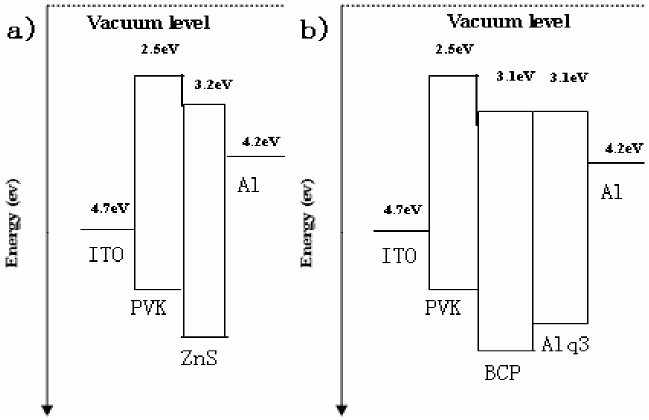

Fig. 2. The energy level diagram of the combined structural device is shown in (a), that of pure organic structural device is shown in (b).

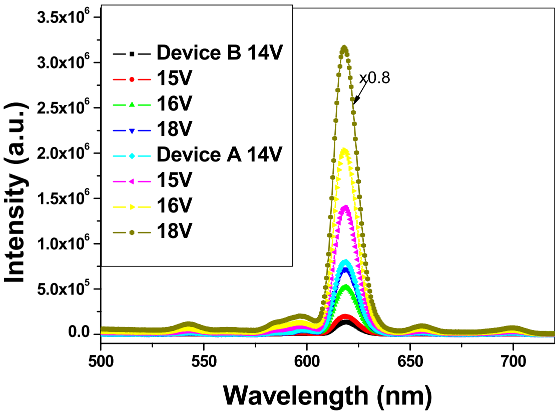

Fig. 3. EL spectra of device A and B under different driving voltage (The comparison of relative EL intensity under different driving voltage is valid for the same device. But it is invalid for different devices because the measured conditions, such as relative position between device and photoelectric detector and the size of the slit, can't be kept constant for different devices).

In the both structural devices, the characteristic emissions of europium ions at 594 nm, 615 nm, 655 nm and 690 nm are obtained under different driving voltage, as shown in Figure 3. These emission peaks are corresponding to four energy level transitions of $^5D_0$–^7F_j (j = 1, 2, 3, 4) of europium ion (Eu^{3+}), respectively. The $^5D_0$–$^7F_1$ is magnetic dipole transition; $^5D_0$–^7F_j is an electric dipole transition whose intensity is sensitive to chemical environment. While the Eu ions are found at symmetrical center, $^5D_0$–$^7F_2$ has strong fluorescence emission.

The EL intensity dependence on the driving voltage is obtained by using the time-base spectra. In the combined structural device, EL intensity abruptly increases when the driving voltage goes beyond 17 V, as shown in Figure 4.

Why is the maximum EL intensity improved in the organic-inorganic combined devices compared with the pure organic structural device? We must analyze the

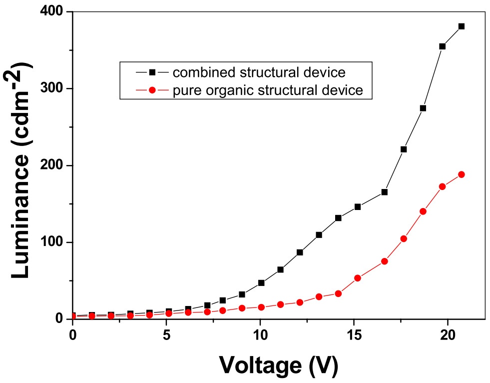

Fig. 4. EL luminance dependence on the driving voltage.

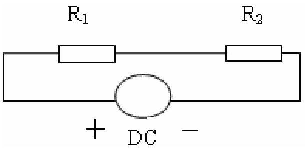

Fig. 5. Equivalent circuit of electroluminescence device.

difference of the current density, the distribution of the internal electric field strength and the excitation mechanism for the two types of structural devices.

3.1 Distribution of electric field strength

First of all, we use an equivalent circuit to describe the distribution of the driving voltage across each layer according to the electric characteristics of the used materials, as shown in Figure 5. R_1 is the resistance of PVK layer and R_2 is the resistance of electron function layer. Here, we neglect the effect of the barrier between the emission layer and the electrons function layer because the barrier is slightly different for the two types of structural devices. So the distribution of the driving voltage should be dominantly determined by charge mobility of these materials. We use the resistance to describe the charge mobility of the material (the faster the charge mobility of material is, the smaller the resistance is).

The EL intensity is dominantly controlled by the electron current density for pure organic structural devices. Because hole mobility of PVK (4.3×10^{-4} cm^2 V^{-1} s^{-1}) is much faster than electron mobility of BCP and Alq$_3$ (1×10^{-6} cm^2 V^{-1} s^{-1} and 6.77×10^{-5} cm^2 V^{-1} s^{-1}) [12,13]. It means that R_1 is much smaller than R_2, so the majority of the driving voltage drops across the BCP and Alq$_3$ layer. For the combined structural device, the electron mobility of ZnS (1×10^2 cm^2 V^{-1} s^{-1}) [1] is much faster than the hole mobility of PVK (4.3×10^{-4} cm^2 V^{-1} s^{-1}). It means that R_1 is much bigger than R_2 and the majority of the driving voltage drops across the PVK layer. In the combined structural device the electric field strength of the PVK layer is much larger than that of electron function layer. It is the contrary for the pure organic structural device. The thickness of the PVK layer is the same for the two types of the structural devices. So the electric field strength of the PVK layer in the combined structural device must be larger than that in pure organic structural device under the same driving voltage.

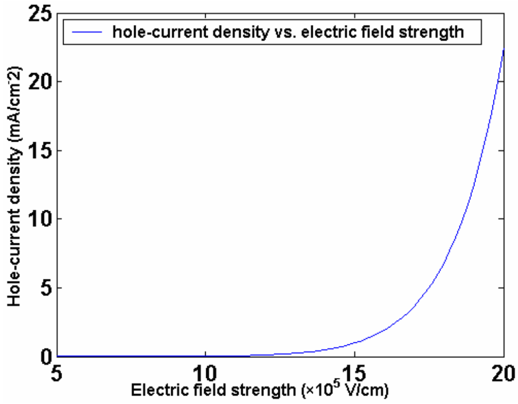

Fig. 6. The dependence of hole-current density in PVK on the electric field strength.

3.2 Current density

Repeated, the charge carrier mobility of organic materials strongly depends on the electric field strength [14–16],

$$\mu = \mu_0 \exp\left(\sqrt{\frac{E}{E_0}}\right), \tag{1}$$

where E is the electric field strength, μ_0 and E_0 are material parameters. The density of the hole current can be described by the following equation:

$$J = nq\, u_0\, E \exp\left(\alpha\sqrt{E}\right), \tag{2}$$

where $n = 10^{11}$ cm^{-3} is the intrinsic carriers density, u_0 denotes the mobility at zero field strength and the coefficient $\alpha = 0.015$ (cm/V)$^{1/2}$ has been given by Gill for PVK [17]. The curve of the hole-current density versus the electric field strength from 5×10^5 to 2×10^6 was simulated by using mathematic software MATLAB according to equation (2), as shown in Figure 6.

The bigger the number of injected holes and electrons is, the bigger is the probability to form exciton. For the combined structural device, the hole current density is increased because the majority of driving voltage drops across the PVK layer. It may be one reason for the improvement of EL intensity of the combined device.

Why is the current of the combined structural device much larger than that of the pure organic structural device, as shown in Figure 7? We must study the electron current and hole current for two types of structural devices. The electron current in the combined device is much larger than in the pure organic structural device due to the drastically different electron mobility. Another important reason is the influence of the electric field strength in the PVK layer on hole current. The electric field strength of the PVK layer in the combined structural device is larger

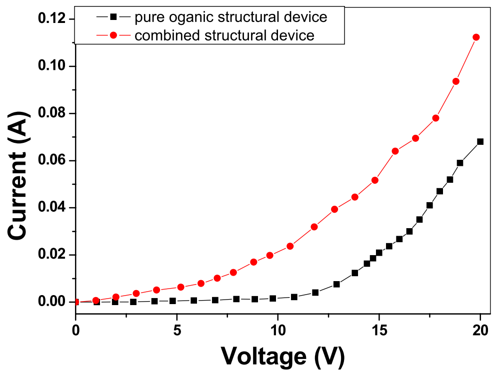

Fig. 7. Current-voltage curve for the two types of structural devices.

than that in the pure organic structural device under the same driving voltage. So the hole current in the combined structural device is larger than that in the pure organic structural device.

3.3 Excitation mechanism

The EL mechanism of lanthanide complex based on pure organic structural devices has been intensively studied [18–20]. The ligand absorbs energy or captures an electron-hole pair and then transfer the energy to Ln ions. We define the process as injected recombination. Injected recombination is the sole excitation mechanism for the pure organic structural device. The Monte Carlo as well as experimental result of vacuum emission spectroscopy shows the presence of high energy electrons up to 6 eV in ZnS [1]. However, the energy distribution of hot electrons in solid state thin film spreads over a wide range. It consists of three parts: simple conduction electrons (n_1), multiplied electrons (n_2) [21], and energetic electrons capable of exciting luminescent center (n_3). These energetic electrons (n_3) which have been accelerated in ZnS layer maintain their number invariant even though they loose their energy during the excitation of lanthanide complex or PVK. Obviously all these three kinds of electrons might recombine with injected holes from the anode. So in the combined structural devices, the excitation mechanism may include impacted excitation and injected recombination. Hot electrons play an important role in terms of EL intensity of lanthanide complex improvement.

4 Conclusions

In the combined structural device, the semiconductor material ZnS thin film is used as an electron function (transporting and acceleration) layer instead of BCP and Alq_3 layers in the pure organic structural device. The majority of the driving voltage drops across the PVK layer because charge carrier mobility of ZnS is much larger than that of PVK. So the hole current density must be increased due to the increase of the electric field strength in PVK layer. These energetic electrons (n_3) which have been accelerated in ZnS layer maintain their number invariant even though they lose their energy during the excitation of lanthanide complex or PVK. There are two kinds of excitation mechanisms: impacted excitation and injected recombination in the combined structural device. For the combined structural device, the EL luminance is strongly improved and reached up to 381 cd/m^2 at 20 V compared with the pure organic structural device.

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