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Blue electroluminescence of ZnSe thin film in an organic–inorganic heterostructures device

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Abstract

Blue light emission of ZnSe thin film from the ZnSe/poly-(N-vinyl-carbazole) (PVK) heterostructures was obtained. The threshold voltage is about 10 V and the brightness of 12 cd/m^2 was obtained at 17 V. From the electroluminescence (EL), the photoluminescence (PL), the transient electroluminescence and the dependence of EL intensity on the applied voltage and current, we attribute the EL of ZnSe to carrier injection and recombination. This new phenomenon not only opens a new mechanism of II–IV compounds in low voltage injection EL but also provides a new way of obtaining blue emission.

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Keywords: ZnSe; Blue emission; Organic–inorganic heterostructures; Injection EL

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1. Introduction

Thin-film electroluminescence (TFEL) plays a very important role for flat plane displays [1]. Nowadays, red and green TFEL displays have been widely used in many fields. Though extensive efforts have been made, an efficient blue device is not completely solved. The lack of an efficient blue phosphor [2] and the impact ionization [3] of the excited state electrons were the hindering block for the development of efficient electroluminescence in the blue. In this Letter, we fabricate a kind of organic–inorganic thin film heterostructures, the organic material poly-(N-vinyl-carbazole) (PVK) as holes transport layer and the ZnSe as the emitting layer. The purpose is to obtain blue TFEL with a new way.

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Over the past years, organic light-emitting diodes (OLED) have been developing very quickly for their potential application in flat panel displays. The mechanism of the organic EL is the injection and recombination of the carriers [4], which is basically identical to that of light emitting diode (LED) of inorganic semiconductors. We noticed that the electric field strength of inorganic EL and organic EL is similar [4–6] and consequent possibility to fabricate a hybrid electroluminescence device from inorganic and organic semiconductors. In general, most polymer materials transport holes preferentially which cause imbalanced carrier injection in organic electroluminescence device, as a result holes may pass through the emission layer without forming excitons with the oppositely charged carriers and lead to ohmic losses. Furthermore, the holes mobility is larger than that of electrons in most organic material, so the recombination zone of holes and electrons is close to cathode where excitons are easily quenched. On the other hand, inorganic semiconductors contain large numbers of carriers and the most important is that most inorganic materials have higher electron mobility. Therefore, some attempts have been done to fabricate organic–inorganic heterostructure taking advantage of both the organic and inorganic materials [7,8]. In fact, high external quantum efficiency (0.4%) and intense luminescence (2000 cd/m^2) have been demonstrated by Coe et al. [9] in an organic–inorganic hybrid device structures combining II–IV semiconductor nanocrystals and conducting polymers. Here, we fabricate a kind of organic–inorganic thin film heterostructures using PVK as hole transport layer to improve the emission of ZnSe and expect to obtain bright, efficient blue EL with a new way.

2. Experiment

In our experiments, poly-(N-vinyl-carbazole) was used as holes transport layer, which was dissolved in chloroform and concentration of PVK is 10 mg/ml. The structure of the hybrid device is shown in Fig. 1. PVK was spin coated onto the ITO (sheet resistance 80 Ω/□), which was thoroughly cleaned by scrubbing, ultrasonic and irradiation in a UV-ozone chamber. The thickness of PVK layer is about 130 nm measured by XP-2 surface profilometer. ZnSe film was deposited by electron-beam evaporation at a rate of 1 Å/s under high vacuum of 2×10^{-6} Torr. The substrate temperature is kept at 150 °C. The thickness of ZnSe layer was 100 nm as measured by a quartz crystal thickness monitor placed near the substrates. Al was prepared by thermal evaporation under a vacuum of 10^{-5} Torr with a thickness of about 200 nm. The EL and PL spectra were measured with spex fluorolog-3 spectrometer.

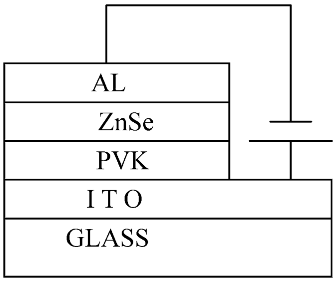

Fig. 1. The structure of the hybrid device.

3. Results and discussion

The EL spectrum of the hybrid device is shown in Fig. 2. The hybrid device was excited under a forward voltage (positive voltage at ITO). The threshold voltage of the hybrid devices is about 10 V, which is lower than that of the single-layer PVK device (ITO/PVK/A1). The brightness of 12 cd/m^2 was obtained at 17 V. There are two emission peaks, one located at 466 nm and the other small shoulder peak located at 407 nm. The current–voltage (I–V) curve of the hybrid and the single layer device were shown in

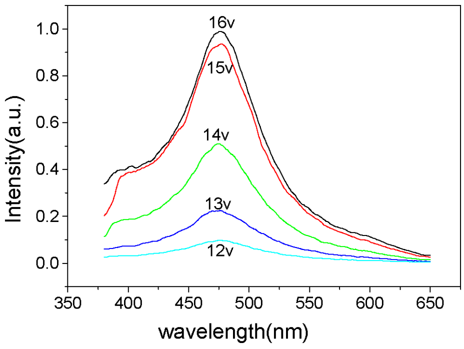

Fig. 2. The EL of the hybrid device.

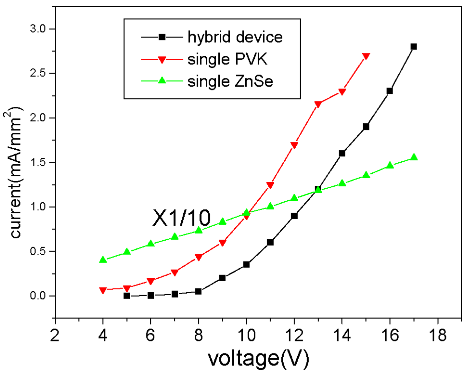

Fig. 3. The voltage–current characteristic of the hybrid device and the single device.

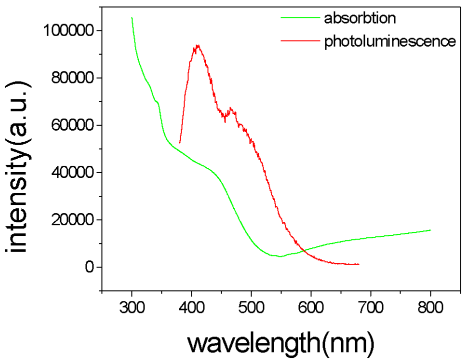

Fig. 4. Photoluminescence and absorption spectra of the device.

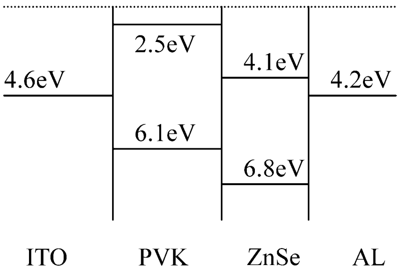

Fig. 5. Energy diagram of the hybrid device.

Fig. 3. The I–V characteristic of the hybrid device is similar to that of the single-layer PVK device. The current of the hybrid device is about several milliampere which is much less than that of the single-layer PVK device and is about one order of magnitude less than that of the single-layer ZnSe device. It means that the I–V characteristic of the hybrid device is dominated by the PVK layer or by the higher electron energy barrier of the interface of ZnSe/PVK. That is to say though the ZnSe layer contain large numbers of electrons, the conductance of the hybrid device is dominated by holes.

To interpret the origin of the blue emission, the absorption and photoluminescence spectra of the device were measured, which was shown in Fig. 4. It is obviously that the absorption spectrum is the overlap of the absorption peaks of PVK and ZnSe. The PL spectrum has two emission peaks. One peak is located at 409 nm, which was the emission of PVK. The other small peak located at 466 nm was attributed to the emission of ZnSe, which was also seen in the ZnSe MIS device and the ZnSe p–n junction [10,11]. And it was attributed to the edge emission of ZnSe. The ZnSe self-activated emission [12] that located at about 560 nm was not observed in this hybrid device. The EL spectrum is partially identical to the PL of the hybrid device indicates that blue emission takes place in the ZnSe layer. The electric field strength of ZnSe layer can be calculated by Maxwell's equations. The resultant equation for the ZnSe layer electric field strength is

$$E_p = \frac{\varepsilon_i}{\varepsilon_i d_p + \varepsilon_p d_i} V_{\text{tot}},$$

where ε is the dielectric constant, d is the layer thickness, and the subscripts i and p represent the PVK and the ZnSe, respectively, V_{tot} is the voltage across the total hybrid device. Here the dielectric constant of PVK and ZnSe are 2.3 and 8.5, respectively, the thickness for PVK and ZnSe layer are 130 nm and 100 nm, respectively. It is easy to know that the electric field strength of ZnSe layer is about 1.7×10^5 V/cm, which is smaller than the electric field strength of conventional inorganic EL (usually more than 1 MV/cm) [13]. And it is difficult for electrons in ZnSe layer to obtain sufficient energy to excite ZnSe by impact excitation. That is to say the emission mechanism of our hybrid device is not the impact excitation.

The energy diagram of heterostructure is shown in Fig. 5. Under a forward voltage, the electrons and the holes are injected from cathode and anode, respectively. At the interface of ZnSe/PVK, the barrier potential for hole is about 0.7 eV while the barrier potential for electron is about 1.6 eV [14,15]. That is to say few electron can inject from the ZnSe layer into the PVK layer. Electron is confined in the ZnSe layer. So the recombination zone of electron and hole is pri-

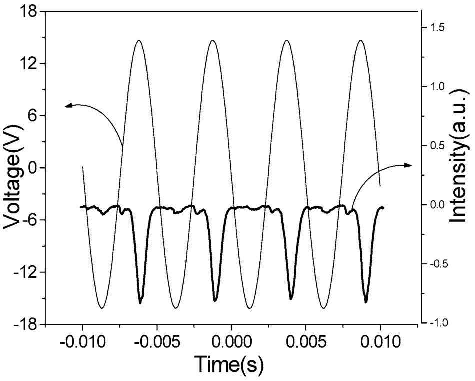

Fig. 6. The transient electroluminescence of the hybrid device.

mary restricted in the ZnSe layer. This is one of the reasons that the emission from PVK was weakly even in enough high forward voltage. In other words, the EL mechanism of the hybrid device is the carriers injection and recombination, which is basically identical to that of OLED. To further investigate the emission mechanism, transient electroluminescence of the hybrid device was measured. Here sinusoidal applied voltage was used. The emission waveforms and the voltage waveforms, as shown in Fig. 6, were recorded by oscillograph. The emission from ZnSe can be observed only when voltage was positively biased. Under a negatively biased, holes injection from Al to ZnSe is difficult because of the high barrier potential at the Al/ZnSe interface (about 2.6 eV). The absence of holes injection precludes the possibility of emission when the sample is negatively biased. In fact, we had prepared another hybrid device: ITO/MEH-PPV/ZnSe/AL, where ZnSe as electron transport layer and MEH-PPV as emission layer. The emission was from MEH-PPV and the emission from ZnSe was not observed. This is also explained by large energy barrier (about 1.7 eV) for hole in the MEH-PPV/ZnSe interface that almost no holes can inject into the ZnSe. That is to say the barrier potential of the interface plays a critical role in this injection type electroluminescence device.

The emission mechanism of this organic–inorganic hybrid heterostructure device is different from device to device [8,16,17]. That is to say by utilizing different organic or inorganic materials, changing the thickness of organic and inorganic layers or adjusting the relative height of barrier potential at organic–inorganic interface, we can tune the emission zone and obtain different emission from each layer. According to the Fowler–Nordheim tunneling model [18], electrons injection from cathode in the hybrid device was divided into two steps: electrons first traverse the barrier about 0.1 eV at Al/ZnSe interface then traverse the barrier about 1.6 eV at the interface of ZnSe/PVK. So, few electrons can inject into PVK layer and most electrons are accumulated at the interface of ZnSe/PVK. Thus reduce the electric field in the cathodic zone (the ZnSe layer). So the electric field in the anodic zone increases due to the redistribution of field. Then holes injection is more easily in higher field. Thus, more holes are injected into the ZnSe layer. The balance of carrier injection is improved.

4. Conclusion

We have obtained blue EL of ZnSe thin film using an organic–inorganic heterostructure with ZnSe as emission layer and PVK as holes transport layer. The EL mechanism of the hybrid device is the injection and recombination of the carriers, which is basically identical to that of OLED. The EL emission at 466 nm is come from the ZnSe layer. Our primary results open the possibility of using II–IV compounds in low voltage injection EL and provide a new way of obtaining blue emission using an organic–inorganic heterostructure.

Acknowledgements

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