Vol 15 No 6, June 2006
1009-1963/2006/15(06)/1370-04

Chinese Physics

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n-type ZnS used as electron transport material in organic light-emitting diodes*

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(Received 21 November 2005; revised manuscript received 9 January 2006)

This paper reports on the n-type ZnS used as electron transport layer for the organic light-emitting diodes (OLEDs). The naphthyl-substituted benzidine derivative (NPB) and tris (8-hydroxyquinoline) aluminium (Alq_3) are used as the hole transport layer and the emitting layer respectively. The insertion of the n-type ZnS layer enhances the electron injection in the OLEDs. The study was carried out on OLEDs of structures: indium–tin-oxide (ITO)/NPB/Alq_3/ZnS/LiF/AL, ITO/NPB/Alq_3/LiF/AL and ITO/NPB/Alq_3/AL. The luminance and efficiency of the device containing this electron transport layer are increased significantly over those obtained from conventional devices due to better carrier balance.

Keywords: OLEDs, n-type ZnS, electron transport layer, luminance, efficiency
PACC: 7860F, 7280L, 7200

1. Introduction

The organic light-emitting display has attracted much attention because it exhibits the advantages of low power consumption, high brightness, high contrast, and low cost.[1−3] The widely used archetype of organic light emitting diodes (OLEDs) based on small active molecules is a device having the following structure: ITO/NPB/ Alq_3/LiF/AL. In this kind of device the Alq_3 is used as both electron transport layer and emitting layer, but the mobility of holes in NPB ($10^{-3}cm^2/V{\cdot}s$) is much larger than that of the electron in Alq_3 ($10^{-5}cm^2/V{\cdot}s$) so that the injection and transport of holes is more easy than that of electrons for such OLEDs and the ideal efficiency has not been achieved.[4−7]

So, it is necessary to enhance the electron injection and transport to a higher level to balance the holes and electrons in emitting layer. Insertion of an electron transport layer at the interface of the electrode and the organic layer is one efficient approach.

In this paper, a novel device structure is proposed for the fabrication of more efficient and brighter OLEDs by inserting an n-type ZnS layer at the cathode–organic interface. The electron injection of the device including ZnS layer is enhanced in contrast with the typical device without ZnS layer. The presence of this layer leads to a significant improvement in the luminance and efficiency of the OLEDs.

2. Experimental

Three kinds of structure was investigated: ITO/NPB (40nm)/Alq_3 (40nm)/AL (device I); a device with LiF layer, ITO/NPB (40nm)/Alq_3 (40nm)/LiF (0.4nm)/AL (device II); and a device with ZnS at Alq_3 and LiF/AL interface, ITO/NPB (40nm)/Alq_3 (40nm)/ZnS (3nm)/LiF (0.4nm)/AL (device III).

The devices are fabricated by vacuum-depositions of NPB, Alq_3, ZnS, LiF and AL on top of the oxygen-

*Project supported by the National Natural Science Foundation of China (Grant No 60476005), the Scientific Research Foundation for Returned Overseas Chinese Scholars, the State Education Ministry, the State Key Program for Basic Research of the Ministry of Science and Technology of China (Grant No 2003CB314707), and the Key Project of National Natural Science Foundation of China (Grant No 50532090).

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plasma treated patterned -ITO substrates.

At first the NPB and Alq_3 were deposited by thermal evaporation at a pressure of $10^{-1} - 10^{-2}$Pa. Secondly, the ZnS (in device III) was deposited by thermal evaporation. Layer thickness was controlled by using a quartz crystal thickness monitor. Finally, LiF and AL were deposited on top of the Alq_3 or ZnS layer through a shadow mask to form 12.56 mm^2 pixels. The evaporation rate is about 0.3Å/s for LiF deposition and 0.5Å/s for ZnS deposition and 0.3Å/s for other materials. For comparison these three control devices used in this paper were manufactured simultaneously.

3. Results and discussion

The electroluminescence (EL) spectra of the three devices are shown in Fig.1, which exhibits a peak at 518 nm, characteristic of Alq_3. So it can be confirmed that the recombination zone is in the emitting layer.

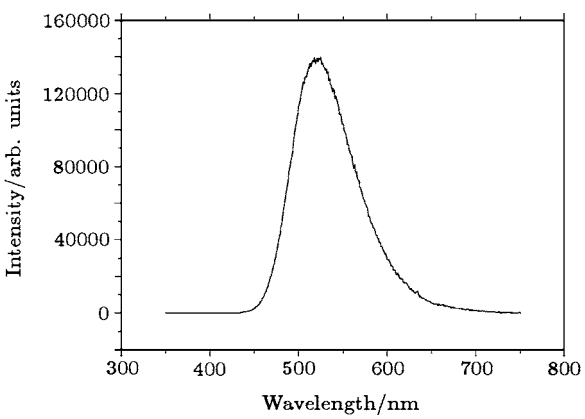


Fig.1. The electroluminescence spectra of these devices.

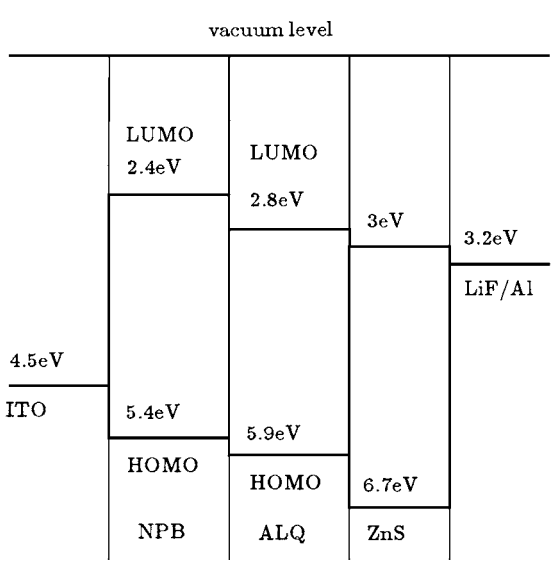


Fig.2. Energy diagram & device structure of device III.

Figure 2 shows the energy level of each layer in device III, the energies of the highest occupied molecular orbital and the lowest unoccupied molecular orbital are shown for NPB and Alq_3.

The current–voltage characteristics of these devices are shown in Fig.3, where the curves I, II and III represent the characteristics of device I, II and III respectively. The data at low voltage (0V–8V) of curves II and III were magnified by 10 times and are shown in the inlet graph. The I–V characteristics in the inlet graph shows that the curve III exhibited a lower drive voltage compared with the curve II. This can be explained by the lower work function and large electron mobility of the n-type ZnS, which can lower the injection barrier and lower the drive voltage. In Fig.3, the curve III exhibits higher current density than that of the curve II at the same voltage. So, it is clear that the insertion of an n-type ZnS layer at Alq_3 and LiF/AL interface can enhance the electron injection and transport of the device. The possible mechanism for this improvement is that the insertion of the n-type ZnS ameliorates the interface of the LiF/Al and Alq_3 and then the electron injection is enhanced. Some papers report that in device II the current in Alq_3 determines the current of the device because the injection of holes is easier than that of the electron. When the n-type ZnS was used as the transport layer in device III the electron injection is enhanced, and then the current density in the device is enhanced.

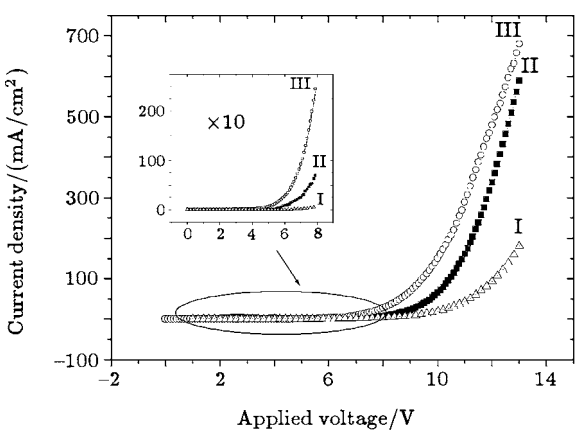


Fig.3. Current density vs. applied voltage for the devices.

The luminance–voltage characteristics of these devices are shown in Fig.4, where the curves I, II and III represent the characteristics of devices I, II and III respectively. The data at low voltage (0V–8V) of

curves II and III were magnified by 10 times and are shown in the inlet graph. It can also be inferred that the drive voltage of device III is lower than device II. In Fig.4 the brightness of device III is larger than device II (by 25% at 13V). Obviously the insertion of a thin ZnS layer at Alq_3 and LiF/AL interface can improve the EL performance of the device. We think that there are two possible mechanisms responsible for the improvement of the device. 1) It is well known that the balance of the transport of holes and electron is very important for the brightness of the device. This means that there should not be large difference between the injection of holes and electron. In device II the injection of holes is easier than that of electron, which will lead to an unbalanced injection. And there are some holes which reach the cathode directly without recombination with electron. When we add an n-type ZnS layer between Alq_3 and LiF/AL the injection of electron is enhanced, a better balance is achieved and the device shows larger brightness.[8] 2) In device III the presence of the ZnS layer can provide a barrier for the holes at Alq_3/ZnS interface. This barrier will block off the holes and keep it in the emitting layer. So, in the emitting layer, the concentration of carrier in the device III is higher than that in device II and the efficiency of exciton formation is increased.

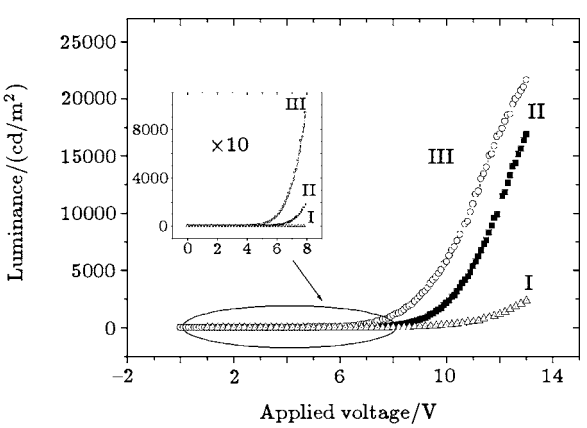


Fig.4. Luminance vs. applied voltage for the devices.

Figure 5 shows the efficiency–voltage characteristics of these devices, where the curves I, II and III represent the characteristics of devices I, II and III respectively. Devices II and III exhibited higher efficiency than device I at the same voltage and device III is the most efficient one: its efficiency is increased by 24% at 8.7V compared with device II. The emissive efficiency had the highest value when a good balance of hole and electron injection was achieved. As we have discussed, the ZnS transport layer can provide a more effective transport of electron and higher exciton formation efficiency. Then the increase of emitting efficiency will be understood naturally. As we have seen, the performance of device II and device III is always better than device I, because the work function of the LiF/AL cathode is lower than the AL cathode so that injection of election in these two devices is much easier. According to Fig.2, the work function of ZnS is very close to that of Alq_3 and with the advantage of high recombination efficiency device III with both LiF and ZnS layer equalizes the number of injected holes and electrons at the emissive layer, which results in the best performance in these devices.

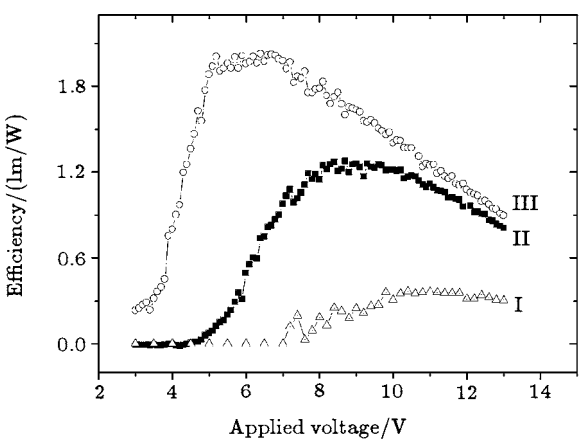


Fig.5. Efficiency vs applied voltage of these devices.

4. Conclusions

We have reported a novel device by using n-type ZnS as electron transport layer. The presence of the n-type ZnS layers results in more effective transport of electron and recombination efficiency, which leads to a significant improvement in the brightness, and efficiency of the OLEDs.

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