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Different emission mechanism of organic–inorganic heterostructure device

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Abstract

Three types of organic–inorganic heterostructure device are fabricated. The emission from the organic layer, inorganic layer and both of the organic and inorganic layers are observed, respectively. The emission mechanism of these organic–inorganic heterostructure devices is different, which can be attributed to the difference of electric field and interfacial barrier of the device. By 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.

Keywords: Organic–inorganic heterostructure; Electric field strength; Impact excitation; Injection

1. Introduction

Up to now there are three kinks of electric field induced luminescence in solids, i.e. light-emitting diode (LED), inorganic electroluminescence (IEL) and organic light-emitting diodes (OLED). The emission mechanisms of these three kinds of luminescence are different from each other; for IEL, it is due to the direct impact excitation [1] of luminescent centers by hot electrons, for OLED it is due to charge carrier injection through opposite electrodes and subsequent recombination [2], and for LED it is due to carrier diffusion through p–n junction and subsequent recombination. From the viewpoint of application, IEL and OLED are especially promising for their potential application in flat panel displays. But there are still some deficiencies that hinder their application. The main problem for IEL is the lack of blue colored emission and the inferior efficiency, and for OLED it is the low carrier mobility and low chemical stability of organic materials. In general, most polymer materials transport holes preferentially which cause imbalanced carrier injection in OLED 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 heterostucture [3,4]. Because of the mechanism OLED is basically similar to that of LED of inorganic semiconductors. Additionally, we noticed that the electric field intensities of IEL and OLED are similar [2,5,6]. So it is possible to fabricate a hybrid EL device from inorganic and organic semiconductors. The organic–inorganic hybrid EL device is expected not only to permit a wide range selection of emitter and carrier transport materials but also to provide a new approach to construct high-performance EL device taking advantage of both the organic and inorganic semiconductors such as high photoluminescence efficiency of organic materials and high carrier density, high carrier

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mobility and steady chemical property of inorganic semiconductors. In fact, some high-performance organic–inorganic hybrid EL devices have been fabricated [7]. But the emission mechanism of this heterostructure device varies from device to device [4,8,9], which is somewhat confusing to understand. What factors influence the emission mechanism of the device? And what influence the emission performance of the device? In this paper, we attempt to make clear these questions and look forward to finding the factors that influence the emission performance of organic–inorganic hybrid EL device.

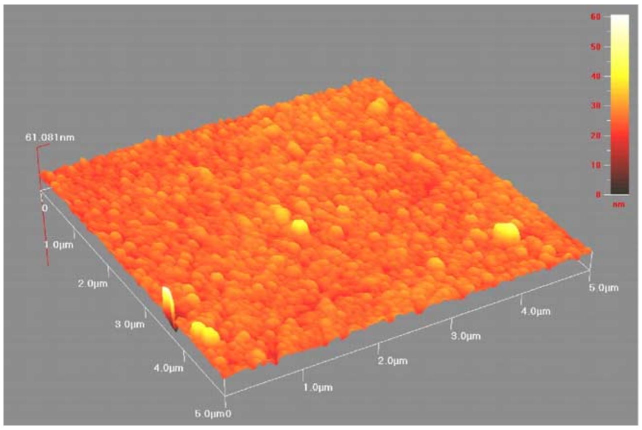

Fig. 1. AFM images of ZnSe surface grown on PVK film.

2. Experiment

We have prepared three kinds of devices: ITO/PVK (130 nm)/ZnSe (100 nm)/AL (device A); ITO/PVK (38 nm)/ZnSe (100 nm)/AL (device B); ITO/MEH-PPV (120 nm)/ZnSe (100 nm)/AL (device C). Here, poly(*N*-vinyl-carbazole) (PVK) was dissolved in chloroform and the concentration was 10 and 3 mg/ml, respectively. The device of our organic–inorganic heterostructure was fabricated as follows: PVK was spin coated onto the ITO (sheet resistance 50 Ω/E), which was thoroughly cleaned by scrubbing, ultrasonic and irradiation in a UV-ozone chamber. The PVK layer thickness was about 130 and 38 nm with different concentration measured by XP-2 surface profilometer. Electron-beam evaporation was used to deposit ZnSe layer at a rate of 1 Å/s under high vacuum of 2×10^{-6} Torr. The substrate temperature is 150 °C. The thickness of ZnSe layer was 100 nm measured by a quartz crystal thickness monitor placed near the substrates. The surface morphology of ZnSe thin film was studied by means of atomic force microscopy (AFM). Al was prepared by thermal evaporation under a vacuum of 10^{-5} Torr with a thickness of about 200 nm. Similarly, we have also prepared the devices C, MEH-PPV dissolved in chloroform and the concentration was 5 mg/ml. The EL and photoluminescence (PL) spectra were measured with spex fluorolog-3 spectrometer.

3. Results and discussion

The surface morphology of as-deposited ZnSe thin film was investigated using AFM (shown in Fig. 1). From the AFM images, it was found that ZnSe film has a grain-like surface morphology. The AFM scanning shows that the maximum value for the peak-to-valley height was 60 nm. But for most part of the sample the peak-to-valley height was about 15 nm. It seems that polycrystalline ZnSe film could be grown onto the PVK layer.

The EL spectrum of the hybrid device A is shown in Fig. 2. When the hybrid device was excited under a forward voltage (positive voltage at ITO), an intense blue emission was observed with a naked eye during the day. There are two emission peaks, one located at 466 nm and the other small shoulder peak located at 407 nm. The threshold voltage of the hybrid devices is about 10 V, which is lower than that of the single-PVK EL device (ITO/PVK/Al). The current–voltage ($I-V$) curve of the hybrid and the single layer device are shown in Fig. 3. The $I-V$ characteristic of the hybrid device is similar to that of the single-PVK device. The current of the hybrid device is about several milliampere which is much less than that of the single-PVK device and is about one order of magnitude less than that of the single-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, although the ZnSe layer contains large numbers of electrons, the conductance of the hybrid device is dominated by holes.

The EL spectrum of device B is shown in Fig. 4, which is drastically different from that of device A. Under a forward bias, the samples exhibit three emission peaks, which can be roughly attributed to characteristic emission of PVK and ZnSe. Besides the edge emission of ZnSe, we also observed the self-activated emission of ZnSe [10] in this device.

The EL spectrum of device C is shown in Fig. 5. The EL device was excited under a dc mode, the emission is observed only at a forward voltage (positive voltage at ITO), and the threshold voltage is about 3 V, which is lower than

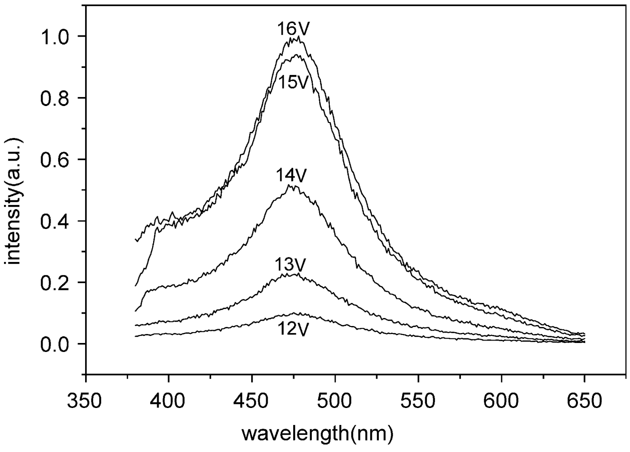

Fig. 2. EL of the device A.

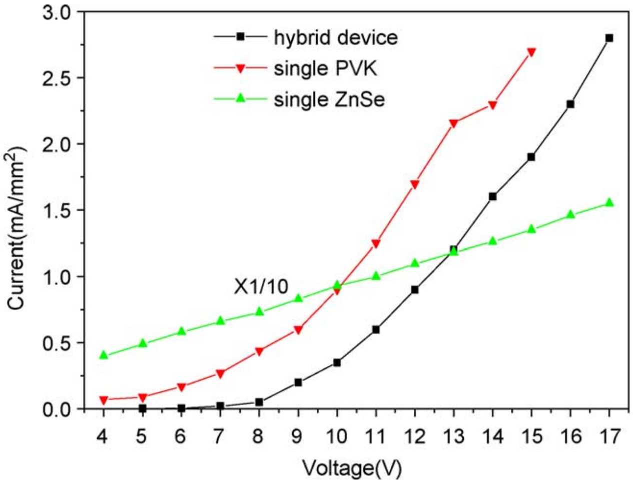

Fig. 3. The current–voltage characteristic of the device.

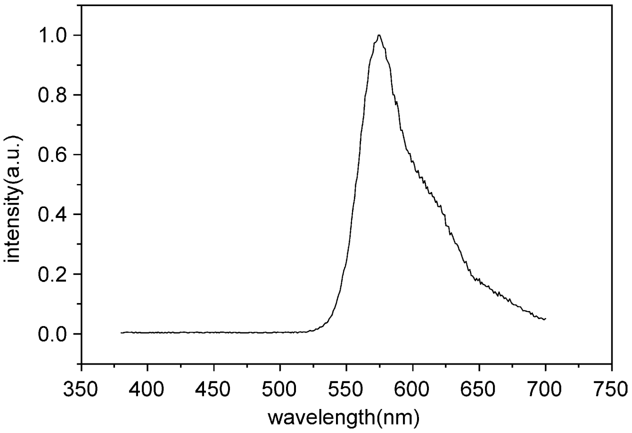

Fig. 5. EL of the device C.

that of the single-layer MEH-PPV device (about 5 V). The brightness of this hybrid device is about several times the same thickness of the single-layer MEH-PPV device. The EL spectrum of the hybrid device is identical to that of the single-layer MEH-PPV device which indicates that the emission takes place in the organic layer and no emission from the ZnSe layer was observed.

To interpret the origin of the blue emission of device A, the absorption and photoluminescence spectra of the device were measured, which was shown in Fig. 6. It is obvious 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 [11,12]. And it was attributed to the edge emission of ZnSe. The ZnSe self-activated emission [10] 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 indicating that the 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

$$E_p = \frac{\varepsilon_i}{\varepsilon_i d_p + \varepsilon_p d_i} V_{tot} \qquad (1)$$

where ε is the dielectric constant, d the layer thickness, the subscripts i and p represent the PVK and the ZnSe, respectively, and 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, and the thickness for PVK and ZnSe layer are 130 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 [13]. So it is difficult for electrons in the 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 device A excited under a forward voltage was shown in Fig. 7. Under a forward

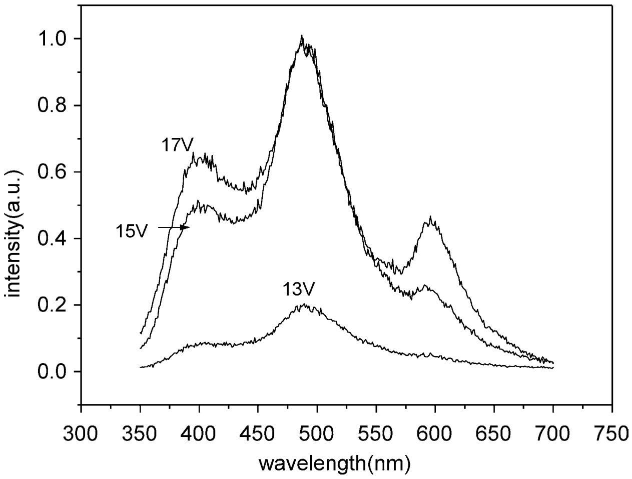

Fig. 4. EL of the device B.

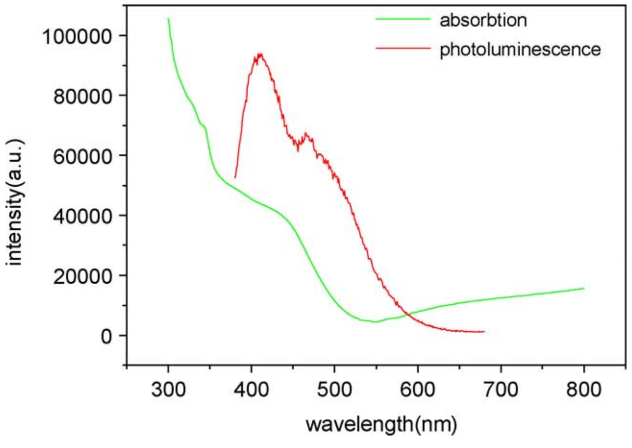

Fig. 6. Photoluminescence and absorption spectra of the device A.

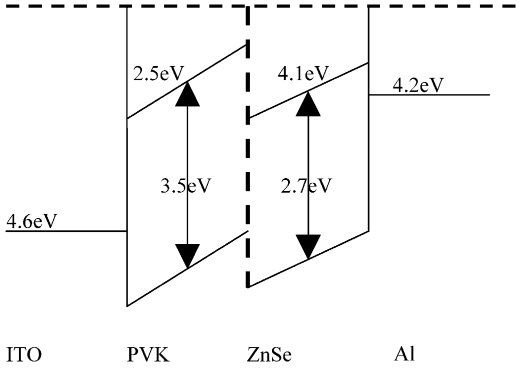

Fig. 7. Schematic band diagrams of device A under a forward bias of voltage V.

voltage, the electrons and the holes are injected from cathode and anode, respectively. Because the electron affinity of ZnSe (about 4.1 eV) is very close to the work function of Al (about 4.2 eV), the energy barrier for electrons injection from cathode into ZnSe layer is only about 0.1 eV, so electrons are very easily injected into ZnSe. 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]. It means that few electrons can inject from the ZnSe layer into the PVK layer. Electrons are confined in the ZnSe layer. So the recombination zone of electron and hole is primarily restricted in the ZnSe layer. This is one of the reasons that the emission from PVK was weak even in high forward voltage. In other words, the EL mechanism of the hybrid device A is the carrier injection and recombination, which is basically identical to that of OLED.

Though the structure of device A and B is similar, the emission spectra of them are drastically different. It is easy for us to think about the electric field strength of the device. According to Eq. (1), the electric strength of the ZnSe layer in device B is about 0.62 MV/cm, which is high enough to accelerate the electrons in conduction band of ZnSe to hot electrons, then these hot electrons have enough energy to impact excite ZnSe and obtain the emission of ZnSe. The voltage–emission intensity ($B-V$) dependence of the edge emission is different from that of the self-activated emission of ZnSe, the emission intensity of the self-activated emission increases more quickly when the applied voltage varied from 13 to 17 V. As to the emission of PVK, it is also easy to understand. As the electric strength of ZnSe layer is higher in device B than in the device A, more electrons can be injected into conduction band of ZnSe; then the number of electrons accumulated at the interface of ZnSe/PVK would increase. The larger the electrons accumulated the more the bending for the energy band at the interface of ZnSe/PVK and the easier for electrons tunneling through the energy barrier from ZnSe layer into PVK layer. On the other hand, the increase of accumulation electrons at the ZnSe/PVK interface will result in a significant redistribution of the electric field, which leads to an enhancement of the anode field. The interface energy barrier establishes an efficient blockade against carrier leakage toward electrodes. The interfacial charge density is comparable to the external capacitor charge and, hence, redistribution of the electric field inside the LED leading to a decrease of the field at the cathode and an increase of the anode field occurs. Since the interfacial carrier densities per unit area Σ is a monotonously increasing function of the injection current [16], it is obvious that there is a significant redistribution of the electric field due to the surplus of electrons that accumulate at an interface with asymmetric blocking efficiency for electrons and holes. And the enhancement of the anode field is larger if electron barrier height at ZnSe/PVK interface is bigger. Since the anode field would increase due to the redistribution of electric fields, holes injection will also increase. Because injection of electrons and holes are also improved, the emission of PVK is increased in device B. That is to say the emission mechanism for PVK and ZnSe layer is different in device B. The emission of PVK results from the recombination of holes and electrons. The emission of ZnSe results from the impact excitation by hot electrons. It means that different types of luminescence can be also integrated into one device structure.

The emission of device C takes place in the organic layer and no emission from the inorganic layer was observed (which is drastically different from that of device A). According to Eq. (1), the electric field strength of ZnSe layer is about 1.2×10^5 V/cm (at the applied voltage of 5 V), which is smaller than the electric field strength of conventional inorganic EL. Therefore, the impact excitation of ZnSe was not observed in device C. Under a forward voltage, the electrons and the holes are injected from cathode and anode, respectively. At the interface of ZnSe/MEH-PPV, the barrier potential for hole is about 1.7 eV. That is to say few holes can inject from the MEH-PPV layer into the ZnSe layer, Holes are confined in the MEH-PPV layer. And the mobility of electrons in ZnSe layer is higher than that of holes in MEH-PPV layer. So the recombination zone of electron and hole is primarily restricted in the MEH-PPV layer. This is the reason that the emission was from MEH-PPV and the emission from ZnSe was not observed in the device C. That is to say that the barrier potential of the interface plays a critical role in this organic–inorganic hybrid electroluminescence device.

According to above results we know that the electric field strength and the barrier potential play a critical role in organic–inorganic heterostructure device. The electric field strength and the barrier could be influenced by each other. The existence of interfacial barrier implies interfacial charge accumulation, which results in a significant redistribution of the electric field. There is a complicated interplay between the electric field-assisted barrier crossing and internal charge accumulation [15]. By 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 emissions from each layer.

4. Conclusion

We have fabricated three types of organic–inorganic hybrid EL device. The emission mechanism of these organic–inorganic heterostructure devices is different, which can be attributed to the difference of electric field and interfacial barrier in the device. By 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 emissions from each layer.

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