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Organic–inorganic hybrid electroluminescence device fabricated by conjugated polymer and ZnS:Mn

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An organic–inorganic hybrid device was fabricated. The architecture of the hybrid device consisted of two layers sandwiched between two injecting electrodes, one of which was a conjugated polymer layer and the other was an inorganic material layer. Emission from both the organic and inorganic layers was observed, but the mechanisms of luminescence for the layers were different. Our primary results suggest the possibility of integrating different types of luminescence into one device structure. © *2000 American Institute of Physics.* [S0003-6951(00)02930-2]

Since the first polymer electroluminescence device (PELD) was reported by the Cambridge group,[1] research on PELD has been developed rapidly due to unique virtues of polymers, namely easy processability, low cost, and the possibility of chemical tailoring to realize desired properties. Light emission in PELD comes from the radiative decay of a singlet exciton formed by the recombination of electron and hole. Generally, high electric field (about 10^6 V/cm) is required for prominent carrier injection and transport.[1] Various methods have been proposed to improve the efficiency of PELD.[2,3] The hybridation of organic and inorganic semiconductors is expected not only to permit a wide range selection of emitter and carrier transport material, but to provide a new approach to construct high performance PELD taking advantage of both the organic and inorganic semiconductors such as high photoluminescence efficiency of organic materials and high carrier density of inorganic semiconductors.[4–7] In fact high quantum efficiency (1%) and long stress life (about 1200 h) have been demonstrated in the organic–inorganic hybrid device utilizing a poly (*p*-phenylene vinylene) (PPV) layer as emission layer and a CdS layer fabricated by the sol–gel method as an electron transport layer.[6]

It is well known that transition-metal or rare-earth–metal ion doped ZnS film shows electroluminescence (EL), and the impact excitation is predominant in ZnS:Mn film.[7] The threshold field strength of EL emission in a single-layer ZnS:Mn device is about 10^6 V/cm,[8] similar to that in PELD, so it is possible to integrate these two kinds of luminescence into one device structure. Our previous results on PPV/ZnS hybrid device showed that the emission from the PPV layer was observed with the significant improvement of luminescent efficiency where the ZnS layer acted as an electron transport layer. By doping the ZnS layer with luminescent activators such as Mn, one can use the electron transport ability of the ZnS layer on one hand, while on the other hand hot electrons in the ZnS layer may excite luminescent activator centers. In this letter we report the organic–inorganic hybrid device fabricated by PPV and ZnS:Mn. Emission from both PPV and ZnS:Mn layers was observed and the mechanism of luminescence for the device was also discussed.

The device was built on indium–tin–oxide (ITO) coated glass slides, which were thoroughly cleaned. PPV film was deposited on ITO substrates by spin casting an aqueous solution of PPV precursor and then thermally converting the precursor film into PPV film at 160 °C in a vacuum oven for 2 h. The thickness of PPV film was measured by a stylus profiler to be 30 nm. The samples were then loaded into a vacuum chamber with a base pressure of 5×10^{-5} Torr. Deposition of a 60-nm-thick ZnS:Mn layer was carried out by electron beam evaporation at a nominal deposition rate of 0.1 nm/s as measured by a quartz crystal thickness monitor placed near the substrates. Aluminum electrodes (about 100 nm thick) patterned by a shadow mask, were thermally evaporated onto the ZnS:Mn layer under a vacuum of 6×10^{-5} Torr. The actual device area was 20 mm^2. All the measurements were carried out at room temperature without subsequent processing. EL spectra of the device were measured by a Hitachi-F4000 spectrometer, and the brightness of the device was measured by the radiance.

EL spectra of the PPV/ZnS:Mn device are presented in Fig. 1. Under the positive bias (i.e., the positive bias on ITO electrode), the EL spectra show two peaks at 505 and 586 nm. The peak at 586 nm is the characteristic luminescence of the Mn^{2+} ion in the ZnS:Mn layer, and the peak at 505 nm is attributed to the light emission from the PPV layer. The EL spectrum can be roughly represented by a superposition of the two individual PPV and ZnS:Mn EL spectra. The ratio of the emission intensity from the PPV layer to that from the ZnS:Mn layer becomes larger with an increase of the applied voltage, but emission from the ZnS:Mn layer is dominant in the whole applied voltage range. Under the negative bias, the EL spectrum is peaking at 586 nm, indicating that only the ZnS:Mn layer contributes to light emission.

Figure 2 shows the current–voltage and brightness–voltage characteristics of the PPV/ZnS:Mn device in a linear representation. As the applied voltage is increased, the cur-

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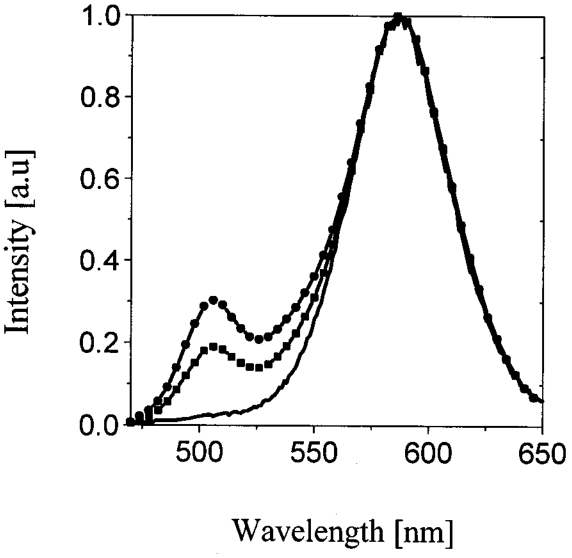

FIG. 1. EL spectra of the PPV/ZnS:Mn device. EL spectra under the positive bias: square (14 V), dots (17 V), and EL spectra under the negative bias.

rent increases in an exponential manner. We note that a similar current–voltage characteristic was also reported in the PPV/CdS device.[6] Compared with the single-layer PPV control device, the onset voltage for a significant current flow was higher and in addition the current was significantly reduced owing to the bulk resistance of the ZnS:Mn layer. The values of electric conductivity for PPV and ZnS:Mn film have been reported to be 5×10^{-9} and 10^{-13} S/cm,[8,9] respectively, moreover in the configuration of the device there was a thicker ZnS:Mn layer. Therefore we conclude that the current–voltage characteristic of the device is controlled by the ZnS:Mn layer. Under the negative bias, the onset voltage was higher and the current was lower in comparison with the case under the positive bias.

Under the positive bias, the threshold of EL emission in this structure was 11–12 V, slightly higher than that in the single-layer ZnS:Mn control device (10 V), indicating that the greater part of the voltage drop was across the ZnS:Mn layer. This further confirms that the current–voltage characteristic of the device is controlled by the ZnS:Mn layer. Under dc excitation, the emission intensity from the single-layer ZnS:Mn control device was very low, consistent with the previous observation.[10] The incorporation of the PPV layer improved the emission intensity from the ZnS:Mn layer. The emission intensity from the ZnS:Mn layer was about 35 cd/m^2 at 17 V. We speculate that the PPV layer may act partly as an ‘‘insulating layer’’ due to the different carrier transport characteristics and low carrier mobility. Under the negative bias, the threshold voltage of EL emission was about 14 V.

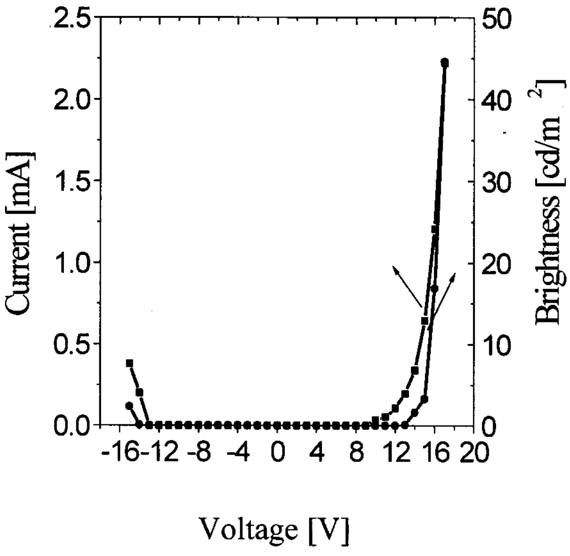

FIG. 2. Current–brightness–voltage characteristics of the PPV/ZnS:Mn device.

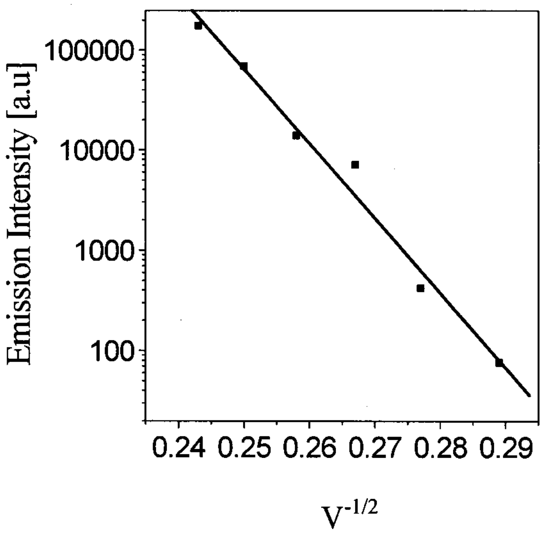

FIG. 3. The emission intensity from the ZnS:Mn layer under the positive bias vs $V^{-1/2}$ characteristic of the PPV/ZnS:Mn device.

Figure 3 shows the emission intensity from the ZnS:Mn layer under the positive bias versus voltage$^{-1/2}$ characteristic in a semilogarithmic representation. The emission intensity is almost linearly decreased with $V^{-1/2}$, indicating that the mechanism of luminescence for the ZnS:Mn layer is the impact excitation (based on the discussion mentioned above we take the approximate value of the applied voltage as that of the voltage drop across the ZnS:Mn layer).[11] To further investigate the excitation mechanism for the ZnS:Mn layer in the device, we incorporated a 10-nm-thick ZnS layer between PPV and ZnS:Mn layers, and found the emission intensity from the ZnS:Mn layer was almost the same as that in the device without the ZnS layer. If light emission from the ZnS:Mn layer in our device is generated by the recombination of holes and electrons, we would observe the emission intensity of Mn luminescent centers dependent on the position of the ZnS:Mn layer in the device. In addition, the results of the PPV/ZnS device indicated that only the characteristic emission of PPV, in other words no emission of defective states in the ZnS layer, was observed in contrast to the case in the PVK/ZnS device, implying that holes were blocked in the PPV layer.[12] Under the negative bias, light emission only from ZnS:Mn layer was observed, which unambiguously demonstrated that reverse-biased EL was resulted from the impact excitation. Two prerequisite conditions, namely the primary electron source and high electric field, are required to make the impact excitation occur. These two conditions can be met in our device since in the PPV

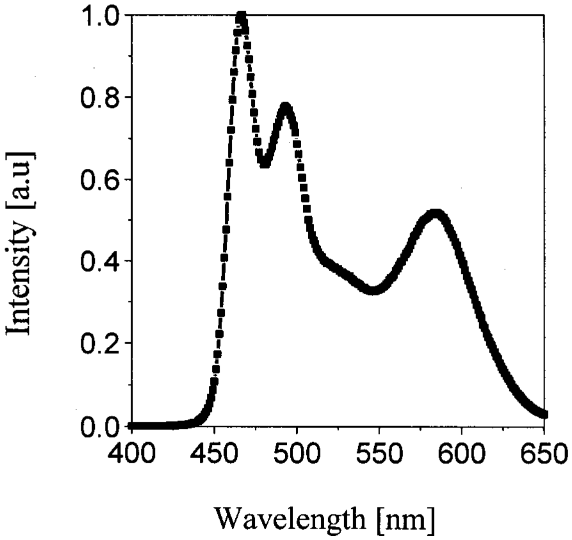

FIG. 4. EL spectrum of the LPPP/ZnS:Mn device.

layer the distance for electron traveling can exceed 50 nm,[13] implying that under the negative bias the electrons injected from the ITO electrode may contribute to the primary electron source. In addition, the interfacial states in the interfaces and the defective states in the ZnS layer may also contribute to the primary electron source. The device can sustain the electric field for the impact excitation. However, relatively weak emission from the ZnS:Mn layer under the negative bias may be attributed to the limited primary electron source due to high electron injection barrier and low electron mobility in the PPV layer. According to the above results we believe that the mechanism of luminescence for the ZnS:Mn layer is the impact excitation. Emission from the PPV layer can only be observed under the positive bias, indicating that in the PPV layer emission came from the recombination of electrons and holes, consistent with the results on the PPV/ZnS device.[12] In particular we note the quantum efficiency of light emission from the PPV layer (0.05%–0.1%) was higher than that of the single-layer PPV control device (0.005%–0.01%), indicating that the inorganic layer also acted as an electron transport layer/hole blocking layer in this device structure.

We propose the mechanism of luminescence for our device as follows: electrons and holes are injected from the electrodes, and the values of barrier height for carrier injection in the material/electrode interfaces are 0.4 eV for holes and 1.2 eV for electrons, respectively. The values of energy levels for the materials used in the experiment are from Refs. 6 and 14. The greater part of the voltage drop is across the ZnS:Mn layer due to high bulk resistance of the ZnS:Mn layer and the redistribution of the applied voltage by the accumulation of holes in the PPV/ZnS:Mn interface for there is a large barrier (1.6 eV) for the injection of holes into the ZnS:Mn layer. Electrons are accelerated in the ZnS:Mn layer and become hot electrons to excite Mn^{2+} luminescent centers. The electrons reaching the PPV/ZnS:Mn interface can tunnel through the barrier (0.4 eV) and recombine with holes in the PPV layer. At a higher applied voltage, the number of electrons in the PPV layer may be enhanced and as a result the emission intensity from the PPV layer increases. Under the negative bias, hot electrons excite Mn^{2+} luminescent centers and only the ZnS:Mn layer contributes to light emission.

By utilizing different organic material and adjusting the thicknesses of organic and inorganic layers, we can tune the emission intensity from each layer. Figure 4 shows the EL spectrum of a ladder (poly-para phenyl) (LPPP)/ZnS:Mn device. In the LPPP/ZnS:Mn device emission from the LPPP layer is dominant.

As a brief summary for this letter, we have demonstrated the organic–inorganic hybrid device fabricated by PPV and ZnS:Mn. Emission from both PPV and ZnS:Mn layers was observed, but the mechanisms of luminescence for the layers were different. Emission from the PPV layer came from the recombination of holes and electrons, while in the ZnS:Mn layer emission was resulted from the impact excitation of Mn luminescent centers. We also observed the improved quantum efficiency of light emission from the PPV layer. Our primary results show the possibility of integrating different types of luminescence into one device structure.

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