Naturally formed graded junction for organic light-emitting diodes

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In this letter, we report naturally-formed graded junctions (NFGJ) for organic light-emitting diodes (OLEDs). These junctions are fabricated using single thermal evaporation boat loaded with uniformly mixed charge transport and light-emitting materials. Upon heating, materials sublimate sequentially according to their vaporizing temperatures forming the graded junction. Two kinds of graded structures, sharp and shallow graded junctions, can be formed based on the thermal properties of the selected materials. The NFGJ OLEDs have shown excellent performance in both brightness and lifetime compared with heterojunction devices. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1605800]

Functional organic thin films have been widely adopted in many interesting organic devices, ranging from light-emitting diodes, transistors, to memory devices.[1–10] In the past decade intensive attention has been paid to organic light-emitting devices (OLEDs) for their potential application in emissive flat panel displays. The most commonly used device structure is the heterojunction structure consisting of an electron transport layer (ETL) and a hole transport layer (HTL) proposed by Tang in 1987.[1] In order to improve the overall device performance, especially the operation lifetime of the devices, the fundamental OLED structures have evolved from sharp heterojunctions[1] to uniformly mixed electron and hole transport materials,[2] and then to graded ETL/HTL structures.[3,4] Recently, a fuzzy-junction structure,[5] which involves a relatively low glass transition temperature (T_g) compound between the ETL and HTL, was also demonstrated. However, most of the graded-junction structures are fabricated by codeposition processes, in which it is difficult to control the distribution of ETL and HTL materials. For example, the graded-junction reported in Ref. 3 requires a repeated process for many sublayers with different ratios of ETL and HTL materials.

In this letter, we describe a method for preparing an organic graded junction. Unlike the previously discussed evaporation process that requires at least two thermal sources (boats), and is complicated to control, this method is a single source process, which means that only one boat is needed and the control of evaporation process is rather simple. This single source evaporation is achieved by evenly premixing the powders of two organic materials, an electron transport material and a hole transport material, and placing this organic mixture into one boat. The remaining evaporation process is similar to the evaporation of organic thin films for traditional OLEDs. Due to the difference in the thermal properties, one material will be evaporated before the other one, and subsequently forms the graded junction. In this letter, we utilize tris-(8-hydroxyquinoline) aluminum (Alq_3) as the electron transport and the emitting material and N,N′-bis-(3-methylphenyl)-N,N′-bis-(phenyl)-benzidine (TPD) or α-naphthylphenylbiphenyl diamine (α-NPD) as the hole transport materials. The thermal properties of the materials should be considered carefully since the naturally formed graded-junction (NFGJ) structures are strongly dependent on the thermal properties of the two materials. For a good graded-junction formation, the HTL materials should have a higher concentration near the anode side and the ETL material should have higher concentration near the cathode side. Therefore, it is required that the HTL material has higher vapor pressure than the ETL material at the same temperature. In other words, when the mixture of ETL and HTL materials is heated in one boat (or crucible), the initial vapor should contain mainly HTL molecules. After the HTL material has been almost exhausted, the ETL material will become the main component of the vapor. The advantage of this process is that the gradient of the ETL and HTL materials is automatically controlled by the nature of the thermal properties of ETL and HTL materials. We can also consider this process as the phase transformation behavior of a two-component system with a fixed content of each compound under constantly increasing temperature. In this case, some interactions between ETL and HTL materials can also occur, which would be helpful for forming graded-junction structures.

Fortunately the commonly used ETL and HTL materials already possess the desired thermal properties. T_g and melting temperature (T_m) for Alq_3 are about 175 and 412 °C, respectively.[11] T_g and T_m for TPD are about 50 and 170 °C,[12] and T_g and T_m for α-NPD are about 95[13] and 282 °C. Generally, the materials which have relatively low T_g or T_m are likely to have relatively high vapor pressures. Under vacuum, it has been proved by our group that the sublimation sequence for these three materials is TPD, NPD, and Alq_3 in that order. As a result, we can obtain a naturally formed graded-junction by simply mixing Alq_3 and TPD or Alq_3 and NPD in various ratios.

In our experiment the ETL and HTL materials are mixed at about 1:1 weight ratio and are ground into fine powder. In order to investigate the graded-junction structures, we have designed a special substrate transport system and shadow mask such that the organic thin films obtained at different evaporation stages can be investigated independently. A quartz substrate, loaded on top of a metal shadow mask, is
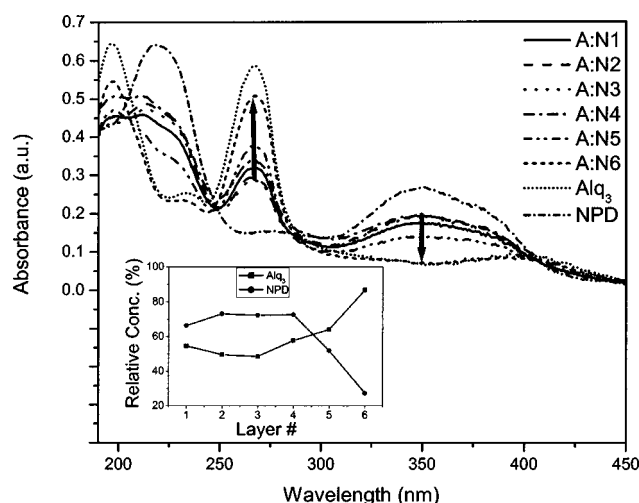
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FIG. 1. Absorption spectra of 30 nm layer for different evaporation stages from single source including Alq_3 and NPD and absorption spectra of pure Alq_3 and NPD 30 nm reference films. (The inset plot shows the relative concentration trends of the two materials. The relative concentrations are estimated by comparing the absorption peak height of each layer with the height of the respective pure reference films.)
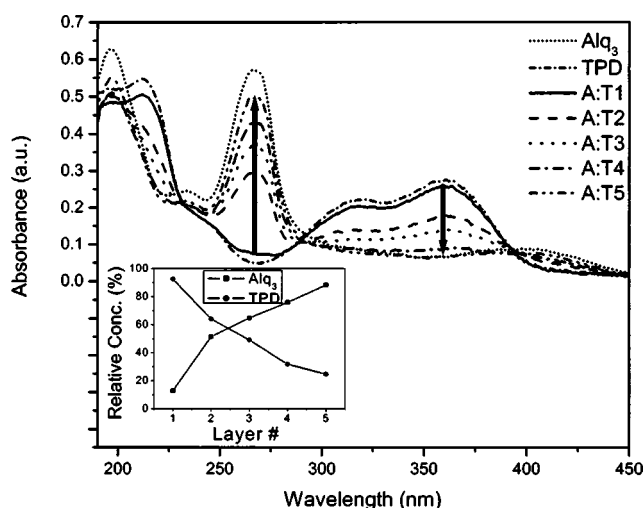

FIG. 2. Absorption spectra of 30 nm layer for different evaporation stages from single source including Alq_3 and TPD and absorption spectra of pure Alq_3 and TPD 30 nm reference films. (The inset plot shows the relative concentration trends of the two materials. The relative concentrations are estimated by comparing the absorption peak height of each layer with the height of the respective pure reference films.)

transportable back and forth by two strings connected to two rotating rods, which can be controlled from outside of the vacuum chamber. By controlling these two rods simultaneously, we are able to move the substrate past the opening of the mask at different stages during the evaporation. Hence, we prepared a series of organic thin films from single source evaporation by moving the quartz substrate sequentially. The vacuum pressure was about 3×10^{-6} Torr and the deposition rates were about 1.5 Å/s. The thickness of each film was 30 nm controlled by a calibrated quartz-crystal monitor. Pure ETL and HTL films were also prepared on the quartz substrates as the references, which can be used to estimate the approximate concentrations of ETL and HTL materials. There are, however, some systematic errors in our system, since we did not consider the nonzero base lines problem and the absorption interference (physical effect or chemical reaction) between these materials and we also ignored the small calibration departure of the quartz-crystal monitor.

Figure 1 shows the absorption spectra of the thin films prepared from Alq_3 and NPD mixed powder from a single evaporation source. In this letter, we defined the film prepared from the mixture of Alq_3 and NPD as A:N, and A:N1 is the first 30 nm layer of the graded structure, A:N2 is the second 30 nm layer, and so on. In the UV-visible absorption spectra, the 268 nm peak is the characteristic peak for Alq_3 and 348 nm is the characteristic peak for NPD. We first calibrate these peak heights of the absorption spectra and film thickness for pure Alq_3 and NPD as the reference. Subsequently, we are able to estimate the relative concentrations of Alq_3 and NPD of each composite film by comparing the peak heights of each compound with the pure materials using the Beer–Lambert law. The inset of Fig. 1 shows the variation in the relative concentrations of Alq_3 and NPD, respectively, from the A:N1 layer to the A:N6 layer. From these results, it is clear that the film prepared from Alq_3/NPD mixed compound is a rather uniformly distributed layer. The mixture ratio is quite steady from A:N1 to A:N4. The relative

concentrations of NPD and Alq_3 have a decisive effect on composition of A:N5 and A:N6, partially due to the exhausted NPD. This set of data suggests that the Alq_3/NPD system is a rather uniformly mixed system, alternatively, it can be considered as a shallow graded junction, in which the variation (gradient) of the concentrations for both compounds is small.

Figure 2 shows the absorption spectra of the thin films prepared from Alq_3 and TPD mixture from a single evaporation source. (We call it A:T film and A:T1 means the first 30 nm layer, and so on and so forth.) Similar to the previous example, the relative concentrations of Alq_3 and TPD in each thin film are estimated by using the 268 nm peak for Alq_3 and the 361 nm peak for TPD, respectively. The inset of Fig. 2 shows the relative concentration trends of Alq_3 and TPD from A:T1 to A:T5. The results indicate that Alq_3/TPD forms a rather sharp graded junction, and it is much closer to a heterojunction structure, unlike the previous example. All these thin films, namely Alq_3/NPD and Alq_3/TPD, show green photoluminescence emission similar to the Alq_3 film, since the energy transfer is efficient between Alq_3 and the hole transport compounds (NPD and TPD).

To verify the usefulness of the NFGJ, OLEDs were fabricated using these two sets of thin films as the active element. For all the OLEDs fabricated, glass substrates coated with indium tin oxide were used as the substrates. The substrates were treated by the UV-ozone process after a careful cleaning process involving sonication of the substrate in alcohol and acetone.[14] To improve electron injection, a bilayer cathode consisting of 5 Å lithium fluoride (LiF) and 1000 Å of aluminum (Al) was used.[15] The device fabrication was carried out under about 3×10^{-6} Torr vacuum and the deposition rates for organic materials, LiF and Al were about 1.5, 0.1, and 7 Å/s, respectively. The repeatability of our devices is good. The film thickness is controlled by the amount of material loaded into the boat, which is weighed precisely prior to device fabrication. The thickness of the graded-junction layers was about 90 nm for the devices reported in
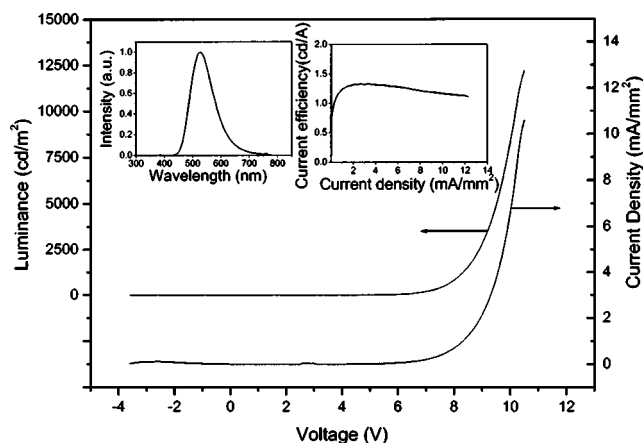
FIG. 3. $I-V$, $B-V$ curves of the NFGJ OLED with Alq$_3$ and NPD. (The inset plots are EL spectrum and efficiency-I curve.)

this letter. The active emitting area of the devices was about 12 mm. The device current density–voltage ($I-V$) curves were measured using a Keithley 236 source-measurement unit controlled by a personal computer. The brightness and electroluminescent (EL) spectra were determined using a Photoresearch 650 photometer.

Figure 3 shows the current density–brightness–voltage ($I-B-V$) curves for the OLED with an Alq$_3$/NPD graded layer and the inset shows the normalized EL spectrum and the efficiency-current curve for the device. Figure 4 shows the $I-B-V$ curves for Alq$_3$/TPD graded layer OLED and the inset plots show the normalized EL spectrum and the efficiency curve for the device. Compared to traditional heterojunction OLEDs, NFGJ OLEDs have almost the same brightness, the same EL spectra and similar diode characteristics but with slightly lower luminescence efficiencies. However, the device operating lifetime for the graded-
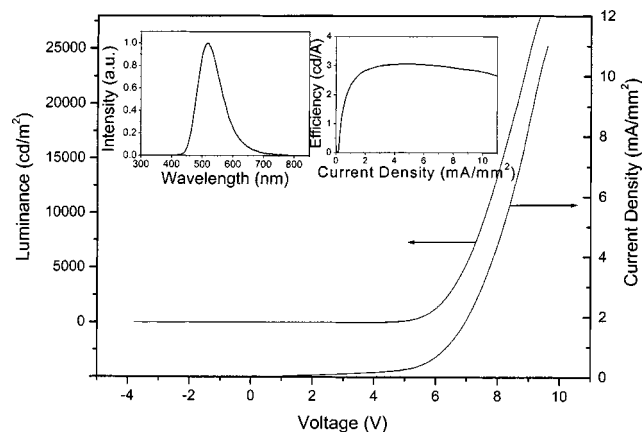
junction device is better than the traditional heterojunction devices. These results are consistent with the results obtained from graded mixed-layer OLEDs.[3,4] Although, the disadvantage of this method is that the materials must be completely consumed for one set of devices. However, this problem can be resolved by automatic materials feeding system for future industrial manufacture.

To summarize, we have invented a method to prepare NFGJ for OLEDs using a single source evaporation process. The gradient distribution of Alq$_3$, TPD, and NPD are systematically investigated using absorption spectra. Based on the thermal properties of the materials, different graded junctions, shallow or sharp, can be formed. Furthermore, OLEDs with NFGJ have also been demonstrated, the performance is comparable to the heterojunction OLEDs, but with better device lifetime. Compared to the traditional multiple source method, this method provides better uniformity. Our NFGJ process utilizes only one evaporation source that eliminates the spatial nonuniformities by combing two (or multiple) sources into one. The method of introducing dopants is still under investigation and will be report separately.[16] In the future, the gradient of material distribution and the junction position can be controlled by materials selection and their relative ratios. It is anticipated that this method will significantly simplify OLED device fabrication, and future manufacturing of large display panels.

FIG. 4. $I-V$, $B-V$ curves of the NFGJ OLED with Alq$_3$ and TPD. (The inset plots are EL spectrum and efficiency-I curve.)

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