Organic electroluminescent diodes

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A novel electroluminescent device is constructed using organic materials as the emitting elements. The diode has a double-layer structure of organic thin films, prepared by vapor deposition. Efficient injection of holes and electrons is provided from an indium-tin-oxide anode and an alloyed Mg:Ag cathode. Electron-hole recombination and green electroluminescent emission are confined near the organic interface region. High external quantum efficiency (1% photon/electron), luminous efficiency (1.5 lm/W), and brightness (>1000 cd/m^2) are achievable at a driving voltage below 10 V.

Organic materials have previously been considered for the fabrication of practical electroluminescent (EL) devices.[1] The primary reason is that a large number of organic materials are known to have extremely high fluorescence quantum efficiencies in the visible spectrum,[2,3] including the blue region, some approaching 100%. In this regard, they are ideally suited for multicolor display applications.

However, the development of organic EL devices has not been successful so far, one reason being that high voltage is generally required to inject charges into organic crystals (e.g., anthracene). In early attempts by Helfrich and Schneider,[4] Dresner,[1] and Williams and Schadt,[5] the drive voltage was on the order of 100 V or above in order to achieve a significant light output. Therefore, the EL device power-conversion efficiency is quite low, typically less than 0.1% W/W, despite the reported high external quantum efficiency of $\sim 5\%$ photon/electron. In an attempt to reduce the drive voltage, Vincett *et al.*[6] used thin organic films of similar materials in their EL devices. They reported EL operation below 30 V. However, the quantum efficiency of their EL diodes was only about 0.05%, presumably owing to the inefficiency of electron injection and the inferior quality of the evaporated anthracene films. Other organic thin-film EL work[7,8] reported similar performance. Another factor for the lack of development is perhaps the question of long-term stability of organic EL diodes. There are very few reported data on the organic EL stability in the literature.[6]

In this letter, we report a novel thin-film organic device with superior EL characteristics. It is efficient and can be driven to high brightness by a low dc voltage. In contrast to most organic EL cells, which use a single layer of organic material sandwiched between two injecting electrodes, our EL diode consists of a double layer of organic thin films, with one layer capable of only monopolar transport. The organic materials were chosen such that the morphological, transport, recombination, and luminescent properties were compatible with the construction and operation of the thin-film EL diodes. In addition, we used a low-work-function alloy prepared by vapor codeposition as the cathode for efficient electron injection.

Figure 1 shows the structure of the present EL cell. The substrate is an indium-tin-oxide (ITO) coated glass with a sheet resitance of about 10–20 Ω/□ (Nesatron™ from PPG Industries). It was cleaned by ultrasonication in a mixture of isopropyl alcohol and water (1:1) and degreased in toluene vapor. The first organic layer (about 750 Å) on top of the substrate is an aromatic diamine[9] of molecular structure shown in Fig. 1. The second organic layer is the luminescent film, about 600 Å. It belongs to a class of fluorescent metal chelate complexes.[10] The specific example shown in Fig. 1 is 8-hydroxyquinoline aluminum (Alq_3). The top electrode is an alloy or mixture of magnesium and silver with an atomic ratio of 10:1. The organic layers, as well as the Mg:Ag electrode, were all deposited by vacuum deposition ($\sim 10^{-5}$ Torr). The substrate was nominally at room temperature and the deposition rates for the organic layers were about 2–5 Å/s. The Mg:Ag electrode was deposited by simultaneous evaporation from two separate sources at a total rate of about 10 Å/s.

The organic diode shown in Fig. 1 can be operated in a continuous dc or pulsed mode. It behaves like a rectifier, the forward bias corresponding to a positive voltage on the ITO electrode. Light emission, seen only in forward bias, was measurable from as low as about 2.5 V. Figure 2 shows the continuous dc current vs voltage (I-V) and the radiance exitance vs voltage (B-V) curves. The shape of the I-V curves for most diodes is relatively independent of the thickness of the diamine layer but strongly dependent on that of the Alq_3 layer, indicating that most of the bias voltage is across the Alq_3 layer. The I-V curve can be fitted to an injection-limited model where the electron current is limited by electron emission from the cathode into the Alq_3 layer. The radiance exitance in mW/cm^2 was measured from a diode with an emit-

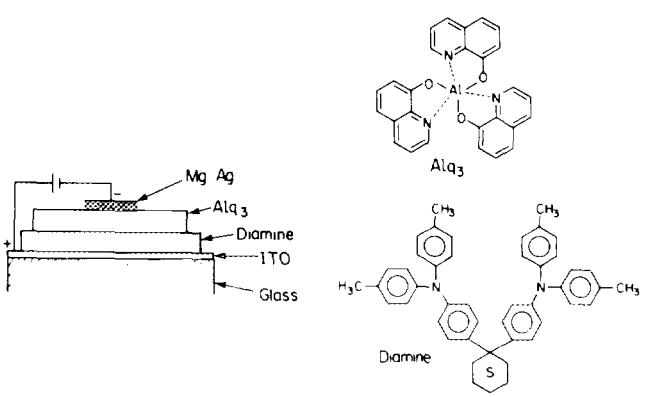

FIG. 1. Configuration of EL cell and molecular structures.

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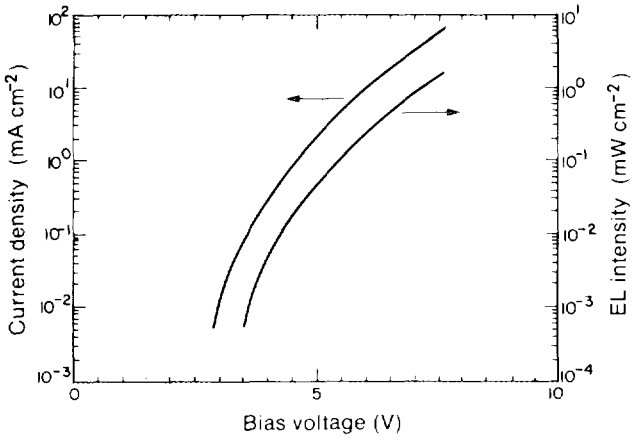

FIG. 2. Brightness-current-voltage characteristics of an ITO/diamine/Alq_3/Mg:Ag EL cell.

ting area of 0.1 cm^2 by a radiometer (EGG model 550-1). The emitting surface is Lambertian for viewing angles within 60° from the normal to the surface. The brightness in units of cd/m^2 was separately measured by a spot photometer (Minolta Luminance Meter, $nt - 1/3°$). A radiance exitance of 0.1 mW/cm^2 is equivalent to a brightness of 100 cd/m^2 for the EL diode with Alq_3 as the emitter. As shown in Fig. 2, the EL diode can be driven to produce high brightness (> 1000 cd/m^2) with a dc voltage of less than 10 V. In pulsed operation, the response of the diode has a rise and decay time on the order of a few microseconds.

The light output from the EL diode is linearly proportional to the input current in the current range from 10^{-1} to 10^2 mA/cm^2. The external quantum efficiency of the EL diode is about 1%. At the power output of 0.1 mW/cm^2, which is visible in ambient lighting, the required drive voltage is 5.5 V and the corresponding power conversion efficiency is 0.46%. The equivalent luminous efficiency is 1.5 lm/W, which compares favorably with the commercially available light-emitting diodes or ZnS-based EL devices.[11]

The emission spectrum of the EL diode is shown in Fig. 3. The peak intensity is at 550 nm, the FWHM is about 100 nm, and the color is green. The EL emission spectrum is independent of the drive voltage or current but is sensitive to the thickness of the organic layers. The latter effect is due to the interference phenomenon of emission in front of a reflecting mirror.[12] For thin organic films (as in Fig. 1) the EL

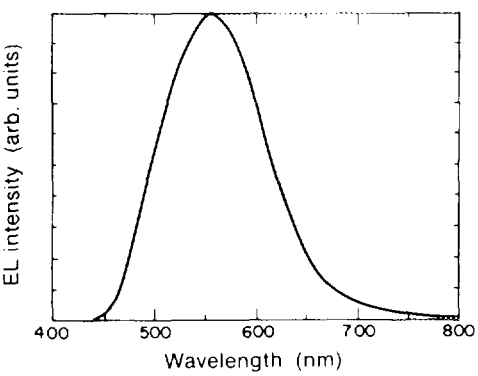

FIG. 3. Electroluminescence spectrum of ITO/diamine/Alq_3/Mg:Ag.

emission spectrum is identical to the photoluminescence spectrum of the Alq_3 thin film. This result indicates that the radiative recombination of injected electrons and holes takes place in the Alq_3 layer. Detailed analysis[13] shows that this recombination is confined to the Alq_3 layer adjacent to the diamine layer to a distance of about 300 Å. The diamine layer, which is known to transport holes only,[9] blocks the electrons injected from the Mg:Ag electrode. Therefore, the interface between the diamine and Alq_3 layer effectively controls the recombination processes.

The morphological properties of the organic layers are critical in the construction of thin-film devices without pinholes. It is necessary that both layers in the EL device be smooth and continuous. The transmission electron micrographs show that the evaporated diamine layer appears to be amorphous, whereas the Alq_3 film is microcrystalline with an average grain size of about 500 Å. The ability to form smooth films in both layers in the present EL diode is related to the low order of symmetry as well as large molecular geometry of the constituent molecules. In addition, the two-layer structure partially alleviates the shorting problem by minimizing the probability of having overlapping pinholes.

The Mg:Ag alloy used as the cathode is important in the reduction of the drive voltage. Mg is a low-work-function metal ideally suited for electron injection into organic materials. However, it is susceptible to atmospheric oxidation and corrosion. The incorporation of Ag in the Mg:Ag film is found to retard these degradation processes. In addition, Ag improves the sticking coefficient of Mg on the organic film during vapor deposition. Other common cathode materials such as In, Ag, and Al generally result in much higher voltage drive and inferior stability.

The EL diode has been tested for stability in a continuous dc operation. Under constant current drive of 5 mA/cm^2 and in an argon ambient, the EL emission (with initial output of about 0.05 mW/cm^2 or 50 cd/m^2) shows a relatively fast degradation in the initial hours (about 30% loss in 10 h) and then decays at a much slower rate to about half of the initial value at the end of a 100-h test. The steady degradation is accompanied by a concomitant increase in the drive voltage from the initial 6 or 7 V to about 14 V during this test period. The nature of degradation is not clearly understood. Some of the failure is attributed to the degradation of both hole and electron injecting contacts, the latter resulting in the formation of dark nonemissive spots.

In conclusion, we have shown a novel organic electroluminescent diode with a double-organic-layer structure. The diode has unique characteristics of high electroluminescent emission efficiency, fast response, low voltage drive, and simplicity of fabrication. It demonstrates that organic materials can indeed be viable alternatives for optoelectronic applications such as displays.

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