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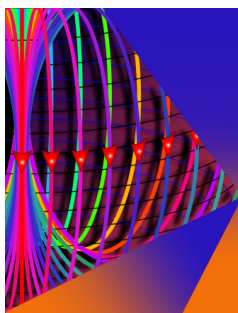


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Enhanced electron injection in organic electroluminescence devices using an Al/LiF electrode

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A bilayer is used as an electrode for organic electroluminescent devices. The bilayer consists of an ultrathin LiF layer adjacent to an electron-transporting layer and an aluminum outerlayer. Devices with the bilayer electrode showed enhanced electron injection and high electroluminescence efficiency as compared with a $\text{Mg}_{0.9}\text{Ag}_{0.1}$ cathode. Similar effects were observed when replacing MgO for LiF. The improvements are attributed to band bending of the organic layer in contact with the dielectrics. © 1997 American Institute of Physics. [S0003-6951(97)04102-8]

There is considerable interest in the use of organic materials for electroluminescence (EL) devices.¹⁻³ To achieve the best device performance, it is desirable to use metals having a low-work function for electron injection into organic materials. However, metals with a low-work function are always susceptible to atmospheric oxidation. For instance, $\text{Mg}_{0.9}\text{Ag}_{0.1}$ is commonly used in EL devices, but shows inadequate corrosion resistance.⁴

For display and optical communication applications,⁵ it is desirable to produce EL devices on a Si substrate containing driver electronics and pixel-switching elements. This configuration requires a surface-emitting EL device with a light transmissive top electrode and a bottom electrode being compatible with the substrate.⁶ With indium-tin oxide (ITO) serving as the top electrode, a low-work function metal would be needed to form the electron-injecting bottom electrode. However, the low-work-function metals are either highly reactive with Si or may act as a fast diffusing species, thus potentially affecting the device performance.

Al is a well-known contact material in Si integrated circuits and exhibits good corrosion resistance, whereas its high-work function precludes the application of Al to low-voltage EL devices. In this letter, we report an Al/LiF bilayer structure, which is useful as an efficient electron-injecting contact to the organic EL device. The presence of a thin LiF layer at the organic-Al interface significantly enhances electron injection. The bilayer is also stable relative to $\text{Mg}_{0.9}\text{Ag}_{0.1}$ and should be compatible with Si device processing.

ITO-coated glass was used as the substrate for organic EL devices. The ITO layer was about 30 nm thick with a sheet resistance of about 100 Ω/square . The routine cleaning procedure included sonication in a detergent, rinsing in deionized water and isopropyl alcohol, vapor degreasing in toluene, and finally irradiated in a UV-ozone chamber. The device has a multilayer structure of Alq/NPB/CuPc/ITO, where CuPc is a buffer layer, NPB is the hole-transport layer, and Alq is the emissive as well as electron-transport layer. All organic layers were prepared by conventional vapor deposition at ambient temperature. The thickness was about 15, 60, and 75 nm, for CuPc, NPB, and Alq, respectively. The top electrode was prepared by sequential deposition of a thin LiF layer and a thick Al overlayer using resistive heating. In some cases, an Al single layer or a $\text{Mg}_{0.9}\text{Ag}_{0.1}$ alloy

layer was prepared for comparison. The EL devices were completed with encapsulation in a dry argon box. Light-current-voltage characteristics were measured using a radiometer and a digital voltmeter. X-ray photoelectron spectroscopy (XPS) was employed to examine interactions of LiF with Alq. The XPS analysis was carried out using monochromatic Al $K\alpha$ radiation, and photoelectron peaks of Li 1s, and F 1s were monitored. Atomic force microscopy (AFM) was employed to study the coverage of LiF on Alq.

Current-voltage characteristics of the EL device with Al, $\text{Mg}_{0.9}\text{Ag}_{0.1}$, or Al/LiF as the cathode are presented in Fig. 1. The device with an Al cathode requires a drive voltage of approximately 17 V to generate a current density of 100 mA/cm^2 , which is substantially higher than that for the device with a $\text{Mg}_{0.9}\text{Ag}_{0.1}$ cathode. The difference is attributed to a higher work function of Al (4.28 eV) relative to Mg (3.66 eV).⁷ The device with Al cathode, however, can be greatly improved by interposing one to two monolayers of LiF between Alq and Al. For instance, the drive voltage at 100 mA/cm^2 was reduced to 10 V with a 0.5-nm-thick LiF layer. Increasing the thickness of the LiF to 1 nm shifts the I - V curve to higher voltages. Other insulating materials were also tested, and the I - V characteristics for MgO and GeO_2 are shown in Fig. 2. Replacing $\text{Mg}_{0.9}\text{Ag}_{0.1}$ by a bilayer of Al/MgO improved I - V characteristics, while interposing a thin

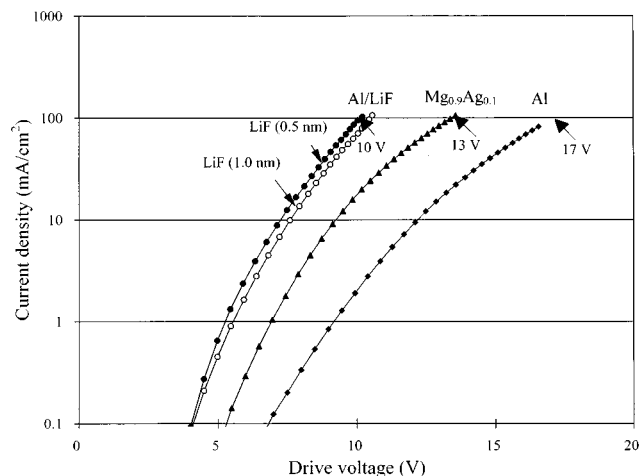


FIG. 1. Current-voltage characteristics of three EL devices using an Al, a $\text{Mg}_{0.9}\text{Ag}_{0.1}$, and an Al/LiF electrode, respectively.

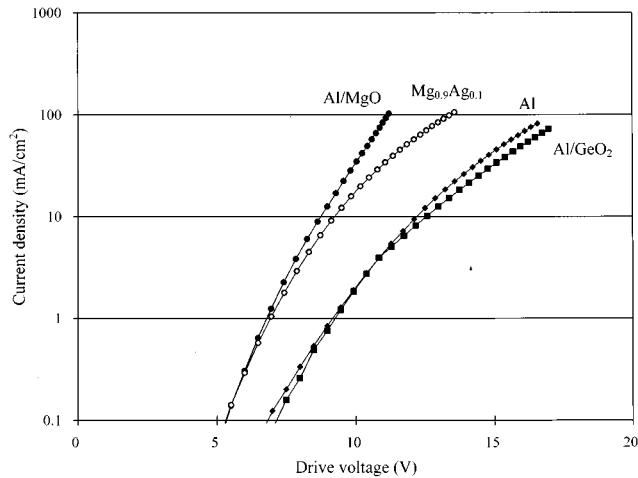


FIG. 2. Current-voltage characteristics of four EL devices using Al, Al/GeO₂, Mg_{0.9}Ag_{0.1}, and Al/MgO electrodes, respectively.

GeO₂ layer between Al and Alq resulted in a shift of the *I*–*V* curves to higher voltages.

Figure 3 shows the EL light output in radiance units vs injected current for three types of cathodes. The light output is directly proportional to the injected current for the current density above 10 mA/cm², and the slope of the curves measures the EL efficiency. The efficiency with a bilayer electrode of Al/LiF is about 0.03 W/A, which is higher than 0.027 W/A with Mg_{0.9}Ag_{0.1} and 0.021 W/A with Al.

For AFM and XPS studies, an Alq thin films with a thickness of 70 nm was evaporated on an ITO-coated glass substrate, and then a 1.5-nm-thick LiF was deposited on the top. AFM images of the LiF/Alq films showed flat surfaces with a mean roughness of approximately 0.75 nm, indicating a good coverage of LiF on Alq. The composition of LiF with an Alq undercoating layer was examined by XPS. The Li 1s and F 1s spectra are shown in Fig. 4, and the peaks can be fitted at 60.1 and 689.7 eV, respectively. A shift of 4.1 eV due to sample charging was determined by referencing the adventitious carbon to 284.8 eV.⁸ Correction for this charging shift gives binding energies of 56.0 eV for Li 1s and 685.6 eV for F 1s, compared to 55.6 and 684.9 eV reported

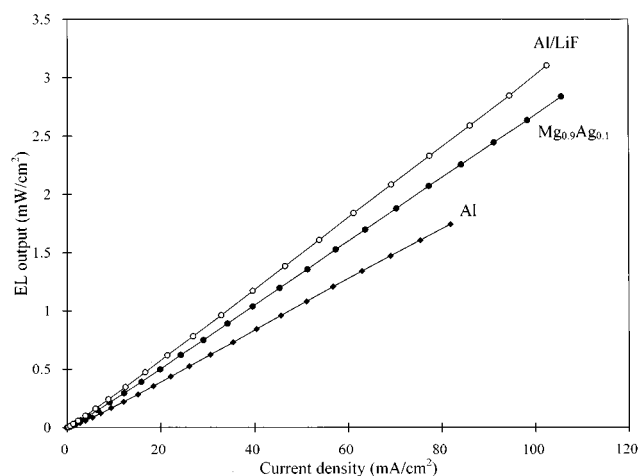


FIG. 3. Light-current characteristics of three EL devices using Al, Mg_{0.9}Ag_{0.1}, and Al/LiF electrodes, respectively.

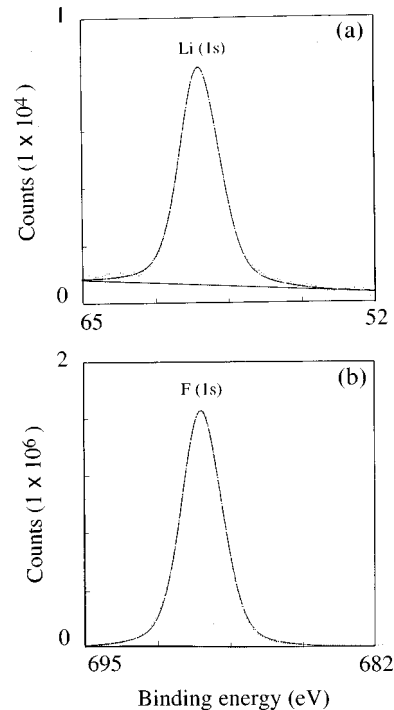


FIG. 4. XPS peaks of (a) Li 1s and (b) F 1s for a 1.5-nm-thick LiF grown on a 75-nm-thick Alq on an ITO-coated glass substrate.

for bulk lithium fluoride.⁸ A more reasonable way to compare the thin film and bulk spectra is to look at the energy separation between the Li and F levels. This method obviates the need to apply corrections for sample charging and gives a value of 629.6 and 629.3 eV for the thin film and bulk cases, respectively. Considering the thin nature of this film and the different instruments used in the measurements, the agreement is excellent. The relative intensities of the F and Li emission peaks agreed well with the bulk. The results clearly indicate that thin LiF layers prepared by thermal evaporation had a stoichiometric composition and did not undergo noticeable dissociation or reaction when coming in contact with Alq.

Li has a low-work function of 2.9 eV, and thus appears to be a good candidate for electron injection into Alq. It has been reported that diluted Li–Al alloys can act as a cathode and exhibit much better *I*–*V* characteristics than a pure Al cathode.⁹ In the present case, the stoichiometric composition of LiF on Alq surfaces unambiguously indicates the absence of any Li metal; therefore, the enhanced electron injection is due to the presence of LiF rather than the low-work function Li.

Lithium fluoride is a superior insulating material because it has the highest band gap energy of 12 eV among oxides and fluorides; however, LiF in the form of ultrathin film backed by an Al layer becomes an effective electron injector. One may attribute the fact to tunneling injection, as sufficient potential difference may be maintained between Al and Alq in the presence of a LiF layer. Tunneling injection has been reported in a Si-based electrode in the form of a thin SiO₂ layer between Alq and heavily doped *n*-type Si.^{10,11} Enhanced quantum efficiency was observed in polymer EL devices through inserting a tunneling barrier.¹² In this work, we

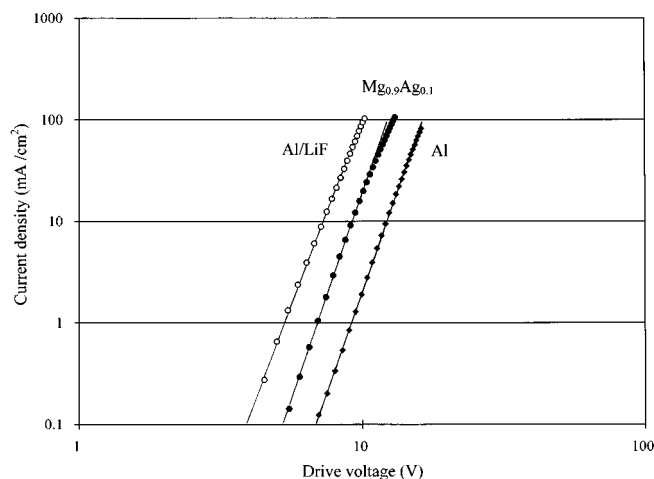


FIG. 5. Fits (solid lines) to the current-voltage characteristics of three EL devices with an Al, a $\text{Mg}_{0.9}\text{Ag}_{0.1}$, and an Al/LiF electrode, respectively.

also observed an improved EL efficiency when using other dielectric materials such as MgO . However, when a GeO_2 layer was used as the insulator, the device performance deteriorated. These results imply that other mechanisms may be operating as well. Our photoelectron emission measurements have revealed that the energy bands of Alq were bent downwards by more than 1 eV when the Alq surface is in contact with LiF, thus substantially lowering the electronic barrier height of the Alq-Al interfaces.¹³ Band bending at metal/polymer interfaces has been reported in the literature,¹⁴ but the degree of bending is considerably smaller.

Burrows *et al.* reported that in organic EL devices with an Alq emitter, the device current is controlled by the trap-limited transport of electrons in Alq, and shows a large power-law dependence on the drive voltage.^{15,16} The dominance of trapped-charge-limited current is only expected in the absence of injection limitation due to the contacts, and the I - V characteristics should be relatively independent of the choice of electrodes. The I - V characteristics of devices with Al, $\text{Mg}_{0.9}\text{Ag}_{0.1}$, and Al/LiF are replotted in Fig. 5, and it can be seen that all I - V curves can be described by $I \sim V^m$ with $m \sim 8$, independent of the contact material. The value of m is within the range reported by Burrows *et al.* The Al-contact device shows no noticeable deviation from the power law, although Al has a much higher barrier than Mg (1.18 vs 0.56 eV) with Alq and the transport of electrons is therefore expected to be injection limited. There is also a parallel shift

in the I - V^m curves, indicating a different threshold voltage for the various electrodes. If the power-law dependence were indeed characteristic for a trap-limited transport process, one would have to assume that the trap density in Alq varies substantially with the electrode properties in order to account for the large separation of the I - V curves. However, this assumption is inconsistent with the picture that the high defect density is a consequence of structural disorder in Alq rather than impurity incorporation.^{15,16} More experiments are required to clarify this issue.

In summary, Al was found to be useful as a cathode for organic EL devices by interposing a thin (~ 0.5 nm) LiF or MgO layer between Al and Alq. Devices with the bilayer electrode show significantly better I - V characteristics and higher EL efficiencies than that with a standard $\text{Mg}_{0.9}\text{Ag}_{0.1}$ cathode. It was observed that the presence of LiF at the Al-Alq interface caused band bending of Alq, thus lowering the electron-injection barrier height.

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