Sodium stearate, an effective amphiphilic molecule buffer material between organic and metal layers in organic light-emitting devices

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Tris (8-hydroxyquinoline) aluminum (Alq_3)-based organic light-emitting devices using an amphiphilic molecule sodium stearate (NaSt) layer between aluminum (Al) cathode and Alq_3 have been fabricated. By comparing the devices with those containing a LiF buffer layer, the results demonstrate that both have almost the same high electroluminescent (EL) brightness but the former is more stable. The amphiphilic property of NaSt is considered as the main reason for this enhancement. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1601675]

Since the demonstration of the first double-layer organic electroluminescent device in 1987,[1] more and more researchers have paid attention to organic light-emitting devices (OLEDs) due to their potential application in flat-panel displays. Although OLEDs have shown sufficient brightness and range of color, some other issues remain critical for practical applications. One such issue is the tight bonding of the metal layer with the organic emitting layer. It is well known that there are many differences in chemical properties between organic and inorganic materials. Because of these differences, organic molecules cannot bond effectively with inorganic molecules. McElvain *et al.* have discovered that Mg easily delaminates from tris(8-hydroxy quinoline) aluminum Alq_3, suggesting its poor adhesion.[2] Some groups have also reported the poor thermal stability[3] and the formation of dark spots at the cathode/Alq_3 interface[2,4,5] in OLEDs due to the incompact structure.

Recently, Cui *et al.*[6] have reported that the interfacial stability of indium-tin-oxide (ITO) anode/OLED hole transfer layer (HTL) could be improved by inserting an amphiphilic molecule {TAA: $[N(p-C_6H_4CH_2CH_2CH_2SiCl_3)_3]$} layer between the ITO anode and HTL using covalent self-assembly. According to this result, the interfacial stability of cathode/organic emitting layer could also be improved by growing such an amphiphilic buffer layer between these two layers. Currently, insertion of a buffer layer[7–11] between the organic emitting layer and the metal cathode layer is used widely, but all the efforts have been aimed at improving the interfacial electronic properties. To our knowledge, improvement of the adhesion by inserting an amphiphilic layer between metal cathode and organic-emitting layers has not yet been accomplished. Here, for growing an amphiphilic layer a molecular-beam deposition method is used in our experiments. An amphiphilic material adopted therein should have certain special properties, including a melting point sufficiently high to make it stable in the OLEDs, and sufficient chemical stability to avoid decomposition during deposition. In this letter, sodium stearate (NaSt: $C_{17}H_{35}COONa$), was selected among many amphiphilic materials as a buffer material between organic and metal layers for bonding these two layers. Compared to devices containing a LiF buffer layer, those containing a NaSt buffer layer demonstrate an improved thermal stability after heating to 80 °C, as well as enhanced electron injection.

The substrate was an ITO-coated glass plate with a sheet resistance of 20 Ω/square. The ITO film was photolithographed as 4-mm-wide stripes. The substrates were washed in an ultrasonic bath of detergent for 30 min, twice in deionized water for 30 min, dried by spinning, and twice treated in ultraviolet-ozone for 5 min.

All layers were fabricated by vacuum deposition at a base pressure of 1×10^{-5} Pa. The whole structure was Al (150 nm)/NaSt ($0 \sim 5.5$ nm) or LiF (0.5 nm is the optimized thickness of the LiF buffer layer[11])/Alq_3 (60 nm)/4,4′-bis[N-(1-naphthyl)-N-phenyl-amino]-biphenyl (NPB, 80 nm)/copper phthalocyanine (CuPc, 20 nm)/ITO/glass. NaSt was evaporated at 320 °C, at a growth rate of $0.3 \sim 0.5$ nm/min. The $I–V$ and luminescence–voltage ($L–V$) characteristics of the OLED were measured using Keithley 236 source measure unit and Keithley 2000-20 multimeter with ST-86LA luminance meter at room temperature under dry nitrogen atmosphere. For the thermal stability experiments, two devices, one with 3-nm NaSt and the other with 0.5-nm LiF, were first placed in a vacuum oven at 80 °C for 1 h then removed and cooled in a glove box under dry nitrogen atmosphere. The $I–V$ and $L–V$ characteristics were then remeasured.

Atomic force microscopy (AFM) was also used to assess the Alq_3/NaSt/Al and Alq_3/LiF/Al interfaces. Because the deposited layers are sufficiently thin, observation of the surface topography using AFM reveals information about the structure of the interfaces beneath. The samples were prepared by vacuum deposition on silicon wafer, and consisted
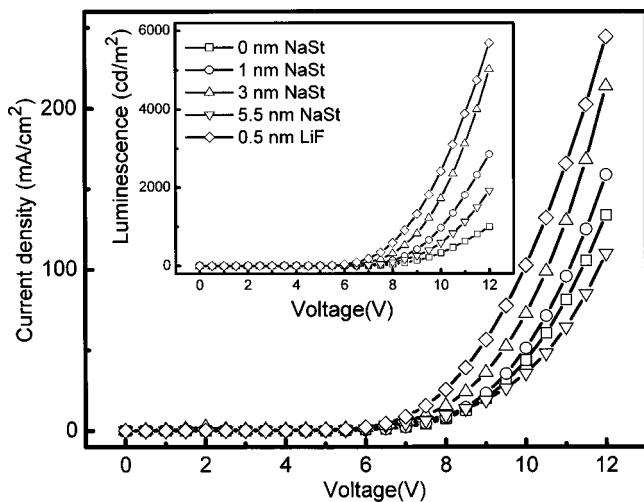
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FIG. 1. The $I-V$ characteristics of a series of device with different thicknesses of NaSt and a device with LiF. Inset: The $L-V$ characteristics of a series of devices with different thicknesses of NaSt and a device with LiF.

of Al (150 nm), NaSt (3 nm)/LiF (0.5 nm), and Alq$_3$ (5 nm), deposited in this order.

The $I-V$ and $L-V$ characteristics of OLEDs that contain the typical thickness NaSt (0, 1.0, 3.0, and 5.5 nm) or 0.5-nm LiF are shown in Fig. 1; Square symbols represent the $I-V$ characteristics of the device without NaSt buffer layer. It is observed that the current density increased by inserting a 1.0-nm (circle) or 3.0-nm (up triangle) NaSt buffer layer. When the thickness of NaSt buffer layer is increased to 5.5 nm, the $I-V$ curve (down triangle) shows that the current density decreased. The $L-V$ characteristics, as shown in the inset of Fig. 1, are very similar to the $I-V$ characteristics.

Figure 2 shows that the current density and luminescence of the OLEDs varies with thicknesses of the NaSt buffer layer at a bias of 12 V. The current density and luminescence are increased by enlarging the thickness of NaSt from 0 to 3.0 nm, whereafter, these values decreased as the thickness is further increased from 3.0 to 5.5 nm. 3.0 nm is hereafter referred to as the optimized thickness. The current density of the device with 3-nm NaSt is comparable with that of the device with LiF. Their values are 214 mA/cm^2 (3-nm NaSt) and 244 mA/cm^2 (0.5-nm LiF), at a bias of 12 V. This indicates that the NaSt can also be used as a buffer layer to improve electron injection and the performance of OLEDs.

To explain the increase in electron injection, several different mechanisms[11–15] have been proposed. Of these mecha-
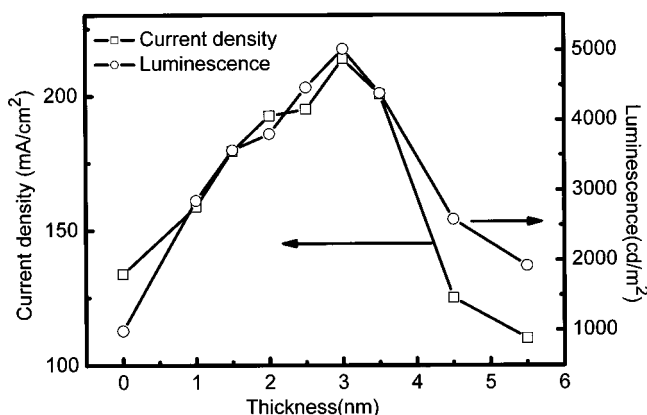

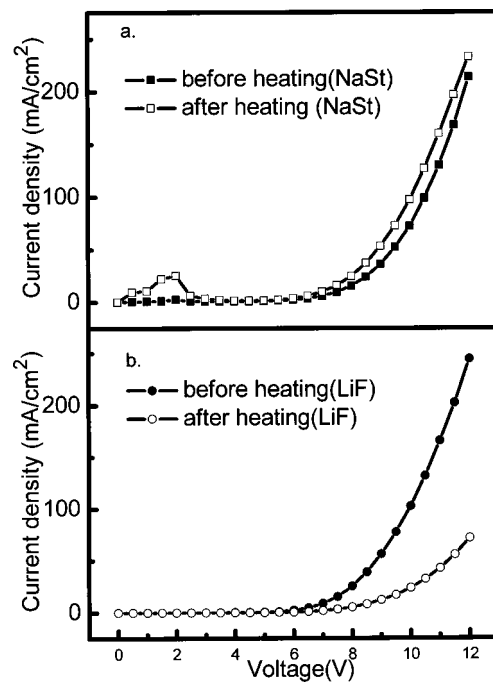FIG. 2. The optimum thickness of the NaSt.

FIG. 3. (a) The $I-V$ characteristics of the device with 3-nm NaSt (before and after heating). (b) The $I-V$ characteristics of the device with 0.5-nm LiF (before and after heating).

nisms, the tunneling model was suitable to interpret our experimental results. According to this model, the enhanced electron injection originated from a lowering of the barrier height due to a repositioning of the cathode Fermi level with respect to the organic lowest unoccupied molecular orbital (LUMO).[15–17] The optimized thickness of the buffer layer is dependent on some parameters of the OLEDs, such as the difference between the conduction band minimum of the buffer layer and the LUMO level of the organic-emitting layer, the resistivity ratio of the buffer layer to organic emitting layer, and the thickness of organic layer. It therefore varies from case to case. The detailed theoretical calculations and experiments about this phenomenon will be described elsewhere.[17]

Besides the current injection, another important issue of OLED performance is the thermal stability. Figures 3(a) and 3(b) show the change in $I-V$ characteristics of the OLEDs containing NaSt and LiF, respectively, before and after the thermal stability test. The curves in Fig. 3(a) represent the $I-V$ characteristic of the OLED with the NaSt buffer layer. One of them with the open square (after heating) is slightly higher than the other with the solid square (before heating). After heating, the current density of OLED containing NaSt at a bias of 12 V increases by almost 10% of the original value (from 214 to 233 mA/cm^2). The luminescence increases from 5016 to 5176 cd/m^2. For comparing the thermal stability with the OLEDs containing NaSt, the OLEDs with LiF was also annealed. The current density drops dramatically after heating, as shown in Fig. 3(b). It decreases to 30% of the original value (from 244 to 72 mA/cm^2 at 12 V). The luminescence drops from 5700 to 1600 cd/m^2. Afterward, the OLED without either NaSt or LiF is heated to the same temperature. At the same voltage, the current density of this device decreases to 23% of the original value (from 134 to 29 mA/cm^2).
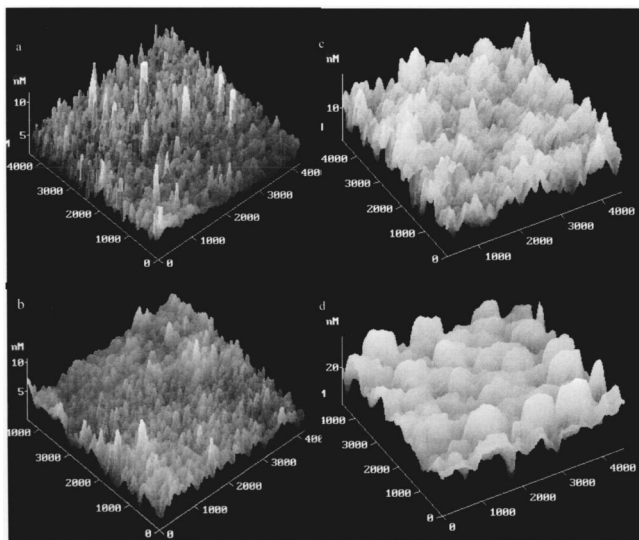
FIG. 4. (a) and (b) AFM image of the Alq3/NaSt/Al interface (before and after heating). (c) and (d) AFM image of the Alq3/LiF/Al interface (before and after heating).

Baran *et al.* recently observed that the vacuum-deposited amphiphilic films, such as stearic acid (HSt) and manganese stearate ($MnSt_2$), showed considerable molecular ordering.[18] In the OLEDs with NaSt, the long lipophilic hydrocarbon "tail" of NaSt should tend to connect with the Alq_3 molecule, and the hydrophilic carboxylic "head" should connect with metal atom of the cathode, stimulating the NaSt buffer layer to bond well with both the inorganic layer and organic layer. Another important character of the NaSt buffer layer is its flexibility due to the long hydrocarbon chain, and this character is a contributing factor to help OLEDs stand up under thermal attack. When the interface between two different materials is heated, the different thermal expansion coefficient will cause the layer structure damage, such as delamination,[19] bend, and curliness.[20] In general, the thermal volume expansion coefficient for organic material is higher than the coefficient for inorganic material.[21] In the cases of OLEDs with LiF buffer layer or without buffer layer, the interface between Alq_3/Al therefore is unstable due to the different thermal expansion coefficient, resulting in a very poor $IV-LV$ characteristic after annealing. In the OLEDs with a flexible NaSt buffer layer, our experimental results show that the thermal stability of the device can be improved by a "flexible connection" between organic and metal due to the elastic hydrocarbons chain of the NaSt molecule. From these experimental results, it is evident that the thermal stability of the OLEDs is strongly related to the metal/organic interface and the flexible connection between organic and metal is a useful way to improve the thermal stability of OLEDs.

Figures 4(a) and 4(b) show the AFM images of the Alq_3/NaSt/Al sample before and after heating, and some changes are observed. It can be seen that the surface of the sample becomes smoother after heating (the Ra roughness is 0.71 ± 0.01 nm before heating, and 0.67 ± 0.01 nm after heating). The Alq_3/LiF/Al interface was also assessed by using AFM. The Ra roughness of this sample is 0.83 ± 0.01 nm before heating and 3.20 ± 0.01 nm after heating, as shown in Figs. 4(c) and 4(d). The work of Park *et al.* shows that the polished ITO can improve electroluminescence and current injection of an OLED, as a result of the increase of the smooth contact area between the ITO surface and the organic layer.[22] In the OLEDs with a NaSt buffer layer, the increase of the electron injection could also be explained in terms of the decrease of the interfacial roughness at Alq_3/Al by the thermal treatment. In the same way, the dramatically increased interface roughness of the OLED containing the LiF buffer layer might be the reason for poor electron injection after heating.

In conclusion, reliability is still the primary issue of industrial research on OLEDs. One cause of degradation of the evaporated devices has been clearly identified: the lack of reliability of the organic–inorganic contacts. We have found that by adding a flexible NaSt buffer layer of suitable thickness between the Alq_3 layer and Al cathode in OLEDs, the thermal stability is significantly improved, as well as the current injection efficiency and electroluminescence output. This flexible connection between organic and inorganic should be of benefit to industry application of the OLEDs.

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