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To cite this article: Bo Jiao *et al* 2009 *J. Phys. D: Appl. Phys.* **42** 205108

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Sodium borohydride as an n-type dopant in tris(8-hydroxyquinoline) aluminium thin film

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Received 11 June 2009, in final form 18 August 2009

Published 2 October 2009

Online at stacks.iop.org/JPhysD/42/205108

Abstract

An efficient n-type dopant, sodium borohydride (NaBH_4), in tris(8-hydroxyquinoline) aluminium (Alq_3) thin film has been developed. Doping NaBH_4 in Alq_3 can significantly enhance the electron injection and transport, which can reduce the applied voltage and improve the efficiency of organic light-emitting diodes compared with the referenced device. Using the quartz crystal microbalance test, we demonstrated that NaBH_4 decomposes following gas formation during the thermal evaporation process. By calculating the deposited fraction of NaBH_4 , we concluded that boron and metallic sodium were the main components of the dopant, while gaseous hydrogen formed during the evaporation process. We thus found that, among these two components, metallic sodium is most likely to be the active component of the dopant because of its strong electron donor characteristic.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, based on different kinds of organic semiconductor materials, significant progress has been made in realizing efficient organic devices such as organic light-emitting diodes (OLEDs) [1–4], organic thin-film field-effect transistors (OTFTs) [5–7] and organic photovoltaic cells [8–11]. Compared with the traditional inorganic semiconductor materials, organic semiconductor materials exhibit some remarkable advantages, such as their potential for low-cost fabrication and large variation of organic chemical structures. However, their carrier concentration and carrier mobility are rather low. Therefore, the optimizations of charge injection and carrier transport play a crucial role in the design of organic electronic and optoelectronic devices.

Electrical doping is an efficient approach for enhancing carrier injection and transport in organic semiconductors, which is similar to inorganic semiconductors. For p-type doping, $\text{F}_4\text{-TCNQ}$ [12–14], a strong electron acceptor, is considered as an ideal p-type dopant which

is extensively used in a variety of materials, such as N, N' -biphenyl- N, N' -bis(1-naphthyl)-(1,1'-biphenyl)-4,4'-diamine (NPB) [13], 4,4',4''-tris[N -(3-methylphenyl)- N -phenylamino] triphenylamine (m-MTDATA) [15], and zinc phthalocyanine (ZnPc) [16]. For n-type doping, the n-type dopants widely used are alkaline metals, such as lithium and caesium [17–19]. However, special equipment is needed to handle those dopants because of their acute reactivity, which is particularly problematic. Thus it is still desirable to find stable and efficient n-type dopants. In this work, sodium borohydride (NaBH_4) was demonstrated to be an efficient n-type doping material in tris(8-hydroxyquinoline) aluminium (Alq_3) thin film. The thermal stability of NaBH_4 during the evaporation process was investigated by the quartz crystal microbalance (QCM) method. By calculating the deposited fraction of NaBH_4 , we conclude that boron and metallic sodium are the main components of the dopant, in which the metallic sodium was supposed to be the active component because of its strong electron donor characteristic. Since NaBH_4 is a cheap and widely used reducing agent, this technology will be beneficial for the development of low-cost organic electronic devices.

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2. Experiments

In our experiments, n-type doping in Alq_3 was realized by the co-evaporation of NaBH_4 and Alq_3 . All the devices were fabricated and measured in the way described in [20]. A series of electron-only devices were fabricated to investigate the electron injection and transport characteristics with a structure of indium tin oxide (ITO)/n-doped Alq_3 layer (100 nm)/Al (100 nm). In devices A, B, C and D, the doping concentrations of NaBH_4 in Alq_3 were 0%, 0.5%, 2% and 5% in volume ratio, respectively. In addition, an undoped device E with a LiF/Al cathode, which is widely used to improve the electron injection in OLEDs, was also fabricated as a reference device. The configuration of device E is ITO/ Alq_3 (100 nm)/LiF (0.5 nm)/Al (100 nm). Both device structures are depicted in figure 1(a). Current density–voltage–luminance (J – V – L) characteristics were measured using a computer-controlled sourcemeter (Keithley 2602) and a calibrated silicon photodiode. All the measurements were carried out at room temperature under ambient conditions. The device used for the QCM test was a regular quartz crystal thickness monitor, which was placed approximately 22 cm above the evaporation boat (a home-made molybdenum boat), and was water cooled to lower the surface temperature. The temperature of the evaporation boat was controlled by adjusting the source current I of the power supply, which was increased by 5 A every 3 min to prevent the material from sputtering during evaporation.

3. Results and discussion

Current density–voltage (J – V) characteristics of the electron-only devices were measured to investigate the doping effect of NaBH_4 in Alq_3 by sweeping the voltage from -10 to 10 V. Figure 1(b) shows the J – V characteristics of the electron-only devices. When the voltage was swept from -10 to 0 V, the ITO electrode acted as the cathode and the Al electrode as the anode, while the ITO acted as the anode and Al as the cathode when the voltage was swept from 0 to 10 V. No matter which electrode acts as the cathode, the ITO electrode for the negative voltage region and the Al electrode for the positive voltage region, all the NaBH_4 -doped devices, B, C and D, exhibit better performance than the undoped device A and device E, as shown in figure 1(b). This result indicates that NaBH_4 doping in Alq_3 can significantly improve the ability of electron injection and transport. The J – V characteristics of the electron-only devices were zoomed in for detailed depiction, as shown in the inset of figure 1(b). It is clear that device C (doped with 2% NaBH_4) shows the highest current density among the five devices at the same applied voltage. For example, at the applied voltage of 10 V, the current densities of the undoped device A and device E with the LiF/Al composite cathode are 1 A m^{-2} and 430 A m^{-2} , respectively. For device B (doped with 0.5% NaBH_4) and device D (doped with 5% NaBH_4), the current densities are 870 A m^{-2} and 350 A m^{-2} , respectively, and for the optimally doped device C (doped with 2% NaBH_4), the current density reaches 4100 A m^{-2} at this applied voltage.

To further demonstrate the n-type doping effect of NaBH_4 in Alq_3 , three OLEDs were fabricated with structures

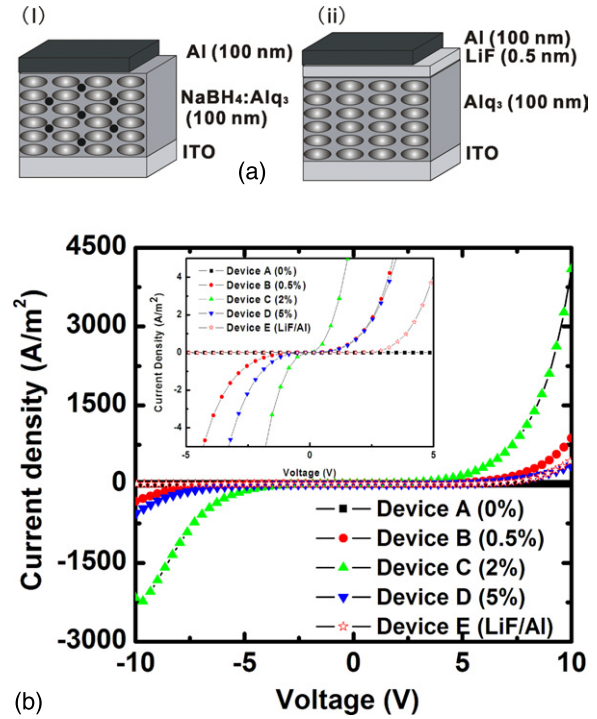


Figure 1. (a) Configuration of the electron-only devices: (i) NaBH_4 doped Alq_3 device (devices A, B, C and D); (ii) Alq_3 device with LiF/Al composite cathode (device E). (b) Current density–voltage (J – V) characteristics for NaBH_4 doped Alq_3 devices (devices A–D). Data for a device with LiF/Al composite cathode (device E) is also shown. Inset shows the zoom-in of the same data in the low-current and low-voltage region.

of ITO/NPB (60 nm)/ Alq_3 (60 nm)/Al (100 nm) (device F), ITO/NPB (60 nm)/ Alq_3 (60 nm)/LiF (0.5 nm)/Al (100 nm) (device G) and ITO/NPB (60 nm)/ Alq_3 (40 nm)/ Alq_3 : 2% NaBH_4 (20 nm)/Al (100 nm) (device H). The configurations of the three devices are shown in figure 2(a). The J – V and L – V curves of devices F–H are shown in figure 2(b), and the characteristics of the current efficiency and power efficiency as a function of the luminance are shown in figure 2(c). Among the three devices, device H with 2% NaBH_4 doped electron-transport layer exhibits the lowest voltage at the same current density, which means doping of NaBH_4 can efficiently reduce the driving voltage of OLEDs, as shown in figure 2(b). As shown in figure 2(c), device H shows higher power efficiency and current efficiency compared with devices F and G. For example, at 1000 cd m^{-2} , the power efficiency of device F is 1.7 lm W^{-1} (3.5 cd A^{-1} at 6.4 V), which is 42% higher than that of device G at 1000 cd m^{-2} (1.2 lm W^{-1} and 2.8 cd A^{-1} at 7.4 V) and 240% higher than that of device F at 1000 cd m^{-2} (0.5 lm W^{-1} and 1.8 cd A^{-1} at 10.8 V). Those data clearly demonstrate that the electron injection is further enhanced by doping NaBH_4 into Alq_3 compared with the conventional LiF/Al cathode. As we know, holes are the major carriers and electrons are the minor carriers [21] in typical bi-layer OLEDs (e.g. device F). One typical method to improve the balance of holes and electrons is to reduce the transport of holes by, e.g., doping rubrene into the hole-transporting layer [22] or doping hole-blocking material, such as bathocuproine (BCP) [23], in Alq_3 . This method, however, will increase the turn-on voltage

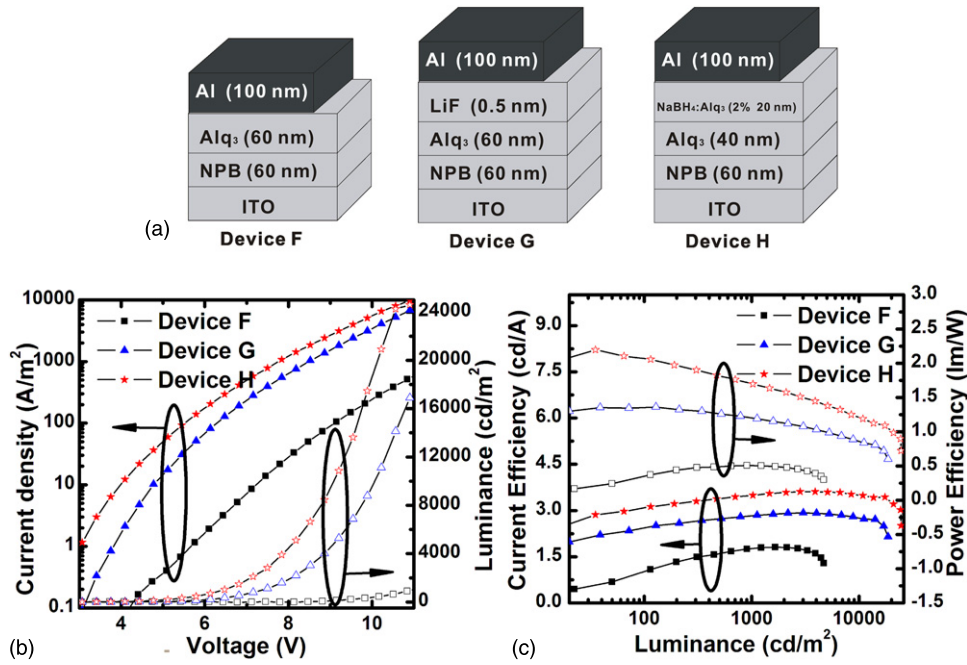


Figure 2. (a) Configurations of devices F, G and H. (b) The current density–voltage (J – V) and luminance–voltage (L – V) curves of devices F, G and H. (c) Current efficiency–luminance and power efficiency–luminance characteristics of devices F, G and H.

of the OLEDs, while increasing its efficiency. An alternative method is to enhance electron injection and transport, such as n-type doping NaBH_4 in Alq_3 , just as demonstrated in the above study of doped electron-only devices. As shown in figures 2(b) and (c), the n-type doping of NaBH_4 in Alq_3 can not only improve the balance between holes and electrons in OLEDs but also reduce the applied voltage of OLEDs, which is important in the practical application of OLEDs.

The QCM test [24–27] was used to evaluate the thermal stability of NaBH_4 during the evaporation process. For a thermally stable material, it is believed that the frequency shift of the QCM (ΔF_S) would be proportional to the mass loss of the boat (ΔM) [26]:

$$\Delta F_S = K \Delta M, \quad (1)$$

where K is a positive constant which is independent of the materials used. While for a material which is thermally unstable, only a fraction ($d\%$) of the mass loss of the boat was deposited during the evaporation, so the frequency shift of the QCM for unstable material (ΔF_{NS}) is given by

$$\Delta F_{NS} = (d\%) K \Delta M. \quad (2)$$

If the mass of the stable and unstable materials that are loaded in the boat are the same, according to equations (1) and (2), the deposited fraction ($d\%$) of the unstable material can be obtained from equation (3):

$$d\% = \Delta F_{NS} / \Delta F_S. \quad (3)$$

In our experiments, NPB, m-MTDATA, LiF and NaBH_4 are used for the QCM test. Among these four materials, NPB, m-MTDATA and LiF are known to be stable during evaporation and are used as in [1, 26]. Figure 3 shows

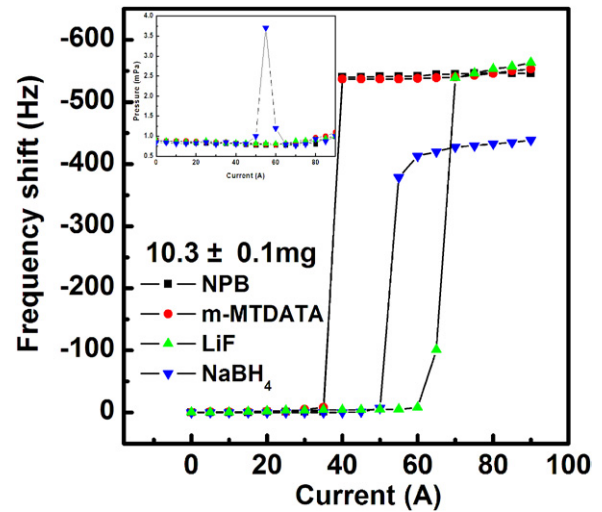


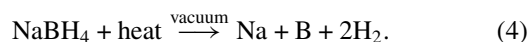
Figure 3. Frequency shift–source current (ΔF – I) curves of NPB, m-MTDATA, LiF and NaBH_4 , respectively, at same amounts of source materials (10 mg). Inset is the change in pressure in vacuum chamber with the increase in source current during the evaporation of NPB, m-MTDATA, LiF and NaBH_4 , respectively.

frequency shift–source current (ΔF – I) curves of NPB, m-MTDATA, LiF and NaBH_4 with the same source mass of 10 mg, respectively. The residual mass after evaporation was less than 1% of the initial amount (10 mg) for NaBH_4 , while almost no residue was observed for the other materials. As shown in figure 3, it is found that the frequency shifts of NPB, m-MTDATA and LiF are almost identical when experimental errors are considered, while NaBH_4 exhibits a much lower shift in frequency than the other materials. From the inset in figure 3, we found that the pressure in the vacuum chamber changed dramatically during the thermal

Table 1. Measured frequency shift (ΔF) and the corresponding deposited fraction ($d\%$). The evaporated weights of all the samples are kept at the same value of 10 mg.

Materials	Frequency shift (ΔF) (Hz)	Deposited fraction ($d\%$) $\Delta F / \Delta F(\text{NPB})(\%)$
NPB	-544 ± 15	—
m-MTDATA	-537 ± 11	99 ± 2
LiF	-563 ± 9	104 ± 2
NaBH ₄	-439 ± 16	81 ± 3

evaporation of NaBH₄, which is in contrast to the evaporation of the other three materials. These phenomena indicate the thermal decomposition of NaBH₄ and the formation of gas. The deposited fraction ($d\%$) of m-MTDATA, LiF and NaBH₄ are calculated and shown in table 1 using NPB as a standard material. The deposited fractions of m-MTDATA and LiF are around 100%, indicating they are thermally stable materials. However, the deposited fraction of NaBH₄ is $(81 \pm 3)\%$, much less than 100%, which indicates that the decomposition of NaBH₄ occurs during evaporation. Ostroff *et al* have reported that NaBH₄ will decompose around 400 °C in vacuum according to the following reaction [28, 29]:



According to this reaction, the theoretical deposited fraction (the ratio of the sum of molecular weight of Na and B to that of the NaBH₄) of NaBH₄ should be 89.4%, which is slightly larger than our experimental value $((81 \pm 3)\%)$. The reason for this minor difference is still under investigation. A possible explanation is that gaseous diborane (B₂H₆) may form during the evaporation, which will decrease the deposition of boron. Therefore, we conclude that the main components of dopant are boron and metallic sodium based on the QCM test and the report of Ostroff *et al*. Metallic sodium has been used as an n-dopant in naphthalene tetracarboxylic anhydride (NTCDA) because of its strong electron donor characteristic (ionization potential = 5.14 eV) [30]. Boron, however, is unlikely to act as an electron donor due to its higher ionization potential, 8.29 eV. So metallic sodium should be the active component of the dopant. These results also help us to understand the dependence of the J - V characteristic of the doped Alq₃ film on the doping concentration of the NaBH₄, as shown in figure 1(b). The current density at all applied voltages increases with NaBH₄ doping because of the existence of the metallic sodium. The optimum doping concentration of NaBH₄ is around 2%. Beyond 2% concentration, the decrease in the current density with doping concentration might be due to the aggregation of boron. A thorough explanation requires experimental investigation of the effect of doping boron in Alq₃, which has not been reported in the literature and is still under investigation.

4. Conclusion

In summary, we have demonstrated an efficient n-dopant, NaBH₄, that was used in doping Alq₃ film. Doping NaBH₄ in

Alq₃ can significantly increase the electron current density and electron injection. This doping technology can further reduce the applied voltage and improve the efficiency of the OLEDs because of the enhanced electron injection and transport. The thermal evaporation process of NaBH₄ has been investigated using the QCM method. By calculating the deposited fraction of NaBH₄, it is concluded that the main components of the dopant are boron and metallic sodium, while the metallic sodium is the active component of the dopant because of its strong electron donor characteristic. Our technology will be beneficial for the development of low-cost organic electronic devices because NaBH₄ is an inexpensive material and its processing is much safer than that of alkaline metals.

Acknowledgments

The authors are grateful to the Ministry of Science and Technology of China (973 program No 2006CB921602), Program for New Century Excellent Talents of the Ministry of Education and the Technology Programme of the Shaanxi Province (No 2006K04-c25) for financial support.

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