Appl. Phys. A 68, 387–390 (1999) / DOI 10.1007/s003399900011

Applied Physics A
Materials
Science & Processing

Impact of the cathode metal work function on the performance of vacuum-deposited organic light emitting-devices

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Received: 7 September 1998/Accepted: 27 November 1998/Published online: 24 February 1999

Abstract. The efficiency of organic light-emitting devices is significantly influenced by the performance of the electron-injecting contact. Lowering the energetic barrier between the metal contact and the lowest unoccupied molecular orbital of the adjacent organic electron transport layer should facilitate the injection of negative charge carriers, and, thus, improve the electroluminescence yield by increasing the electron density in the emitting zone. Therefore, it is widely believed that lowering the work function of the cathode metal will improve the quantum efficiency of the devices and, concomitantly, reduce the operating voltage. Here, we report on measurements of devices with tris(8-hydroxyquinolinolato)aluminum-(III) as electron transport and emissive layer. The latter layer is contacted with a variety of chemically very different cathode metals (including some lanthanides), which cover a range from 2.63 eV up to 4.70 eV on the work function axis. We demonstrate the existence of an efficiency maximum at a work function of about 3.7 eV which, to the best of our knowledge, has not been reported yet. These results are of practical importance with respect to the choice of pure cathode metals for organic electroluminescent display applications.

PACS: 78.60.Fi; 73.61.Ph

Since the first reports on organic electroluminescent devices (OLEDs) using small molecules as hole transporting, electron transporting, and emissive layer [1–4], there has been an increasing interest in the field of OLEDs for display applications. A lot of experimental and theoretical work has been done in order to achieve a more detailed understanding of the underlying physical processes, which plays a crucial role for improving quantum efficiency and operating stability of OLEDs.

One major topic of interest is the electron-injecting contact. This is mostly due to the fact that in many devices holes seem to be the majority carriers [5]. Consequently, balanced charge carrier injection, which is of crucial importance for high quantum yields [6], has not been achieved yet for many device setups. Thus, the electron current from the electron-injecting contact to the emissive recombination zone appears to be the limiting factor for device efficiency. Several models for charge carrier injection from metal electrodes into adjacent organic materials have been described theoretically [7] as well as investigated experimentally [7–9]. One generalized prediction of these different models can be summarized as follows. A reduction of the energetic barrier between the Fermi level of the metal and the lowest unoccupied molecular orbital (LUMO) of the adjacent electron transport material will result in an enhanced electron injection current. Therefore, for cathode metals with very low work functions, the electron-injecting contact should approach ohmic behavior, which has already been achieved for hole injection from indium-tin-oxide (ITO) into various hole transporting materials [10].

In the present paper, we follow a macroscopic approach to shed light on the interplay between the metallic Fermi level on one hand and the energy levels of the adjacent organic materials on the other. For a variety of devices comprising different cathode metals with Fermi levels above and below the LUMO of the adjacent tris(8-hydroxyquinolinolato)aluminum (Alq_3), we will point out correlations of efficiency and onset voltage with the respective metal work function. The investigation of electron-injection mechanisms on a molecular scale is beyond the scope of this work.

Generally, due to their chemical reactivity, low-work-function metals are highly sensitive against moisture and oxygen which implies the necessity for hermetic OLED packaging. From a technical point of view, a compromise has to be found between device efficiency on one hand and packaging demands on the other. Thus, our investigations are relevant with respect to commercial OLED display development.

1 Experimental

For the fabrication of our OLEDs, we used ITO-coated glass slides which were pretreated by thorough solvent cleaning and reactive ion etching in an oxygen plasma. A first layer of N, N′-bis(3-methylphenyl)-N, N′-diphenylbenzidine (TPD) was thermally evaporated (thickness 135 nm, deposition rate 2 Å/s, base pressure 1×10^{-5} mbar), followed by a layer of 65 nm Alq_3 without breaking the vacuum. In order to avoid metal contamination of the organic evaporation sources, the samples were transferred to a separate cathode deposition chamber. Subsequently, the cathode metal under investigation (thickness 150 nm) and an additional protective layer of 150 nm Ag were evaporated on top of the Alq_3 layer (metal deposition rate 10 Å/s, base pressure 1×10^{-5} mbar). No metal with a purity less than 99.8% was used. Sample preparation, transfer, sample handling, and measurements were performed in a glove box filled with purified dry argon (1–10 ppm O_2).

In order to achieve maximum reproducibility and to carefully exclude artifacts, deposition of organic materials was performed on four samples simultaneously, each of them containing eight individual OLEDs (active area 2 mm × 2 mm). The cathode metal deposition on each of the glass slides was performed individually. Out of each series, one standard device, utilizing a Mg cathode, was fabricated. Usually, the maximum luminance of these standard OLEDs was close to 20 000 cd/m^2, validating proper ITO-pretreatment, deposition process control, and material purity. In general, voltage, current and luminance data of our standard OLEDs are consistent with literature data [9, 11]. For maximum data accuracy, all performance parameters given below are values relative to the corresponding data for standard Mg devices.

For electro-optical device characterization, a Keithley source-measure-unit (Model 238) and photodiodes with spectral filters corresponding to the spectral response of the human eye (V_λ filter) were used. The photodiodes were calibrated in terms of luminance with a Minolta luminance meter (Chroma Meter CS-100).

2 Results

In our experiments, we used a variety of cathode metals (Table 1) with very diverse chemical properties. Figure 1 shows luminance–voltage measurements for a selection of these metals. According to these measurements, devices with Mg cathode exhibit the highest slope in luminance. Utilizing cathode metals with higher work functions leads to lower brightness values which is in agreement with theoretical predictions [7]. Surprisingly, we found that devices with cathode metals less noble than Mg also exhibit lower performance.

Figure 2 shows the impact of the cathode metal work function (see Table 1) on OLED performance. As a measure of performance, we used the luminance output at a constant current density of 50 mA/cm^2 (Fig. 2, upper part) [10]. Additionally, the performance in terms of luminous efficiency at a luminance of 1500 cd/m^2 is depicted in the lower part of Fig. 2. At the current density and luminance levels given above, luminance and current are still proportional. Stability and reliability of our devices exceed the measurement cycles by far. However, in the particular case of high work function metals (for example Al) a more pronounced degradation can be observed which has already been indicated by earlier publications [12]. At this point it is worth mentioning that efficient devices (for example Mg standard devices) exhibit a luminance of about 1500 cd/m^2 at a constant current dens-

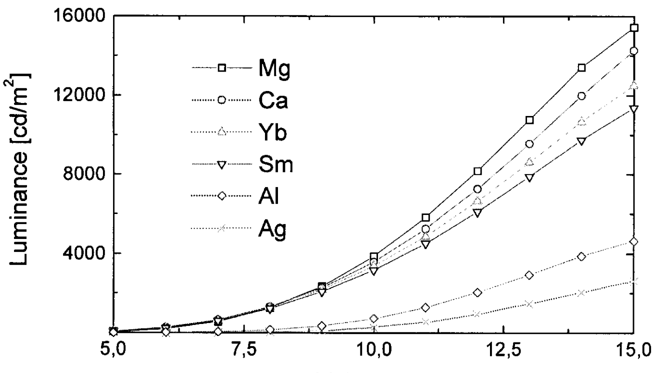

Fig. 1. Luminance–voltage characteristics of devices using a variety of cathode metals. For magnesium cathodes, maximum luminance values close to 20 000 cd/m^2 were typically observed

Table 1. Work functions for various cathode metals used, according to [25]

Element	Work function /eV
Yb	2.63
Sm	2.73
Li	2.95
Ca	3.00
Mg	3.70
Al	4.30
Ag	4.32
Zn	4.47
Cu	4.70

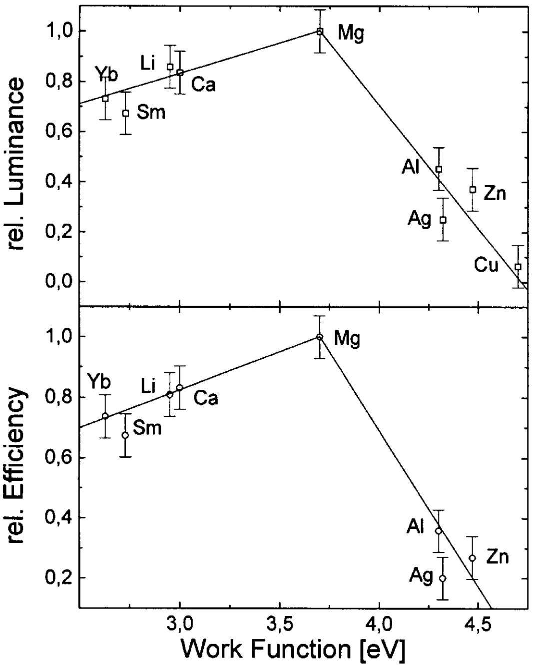

Fig. 2. *Upper part*: relative luminance at a current density of 50 mA/cm^2 as a function of the cathode metal work function. *Lower part*: relative luminous efficiency at a constant luminance of 1500 cd/m^2 as a function of the cathode metal work function. All data shown above are normalized to the corresponding data for Mg cathodes as explained in the text

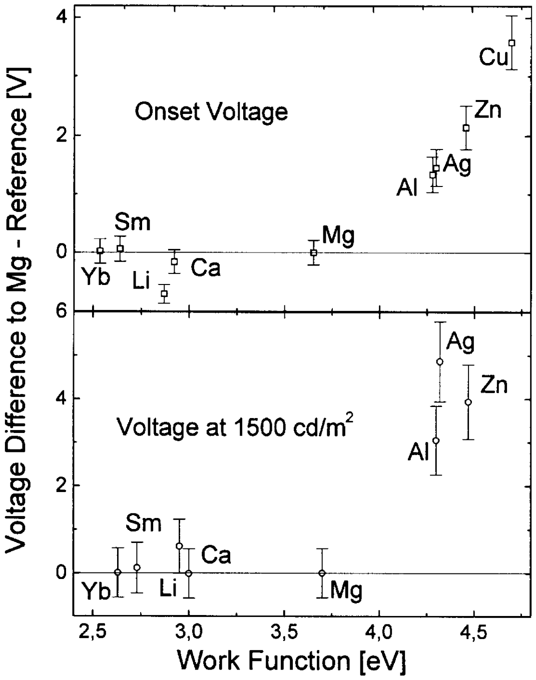

Fig. 3. *Upper part*: impact of the cathode metal work function on the onset voltage (defined here as operating voltage at a luminance of 0.1 cd/m^2). *Lower part*: operating voltage at a constant luminance of 1500 cd/m^2. Again, all data are normalized to the corresponding values for devices with Mg cathodes. For the standard Mg devices, onset voltages lower than 3.0 V and operating voltages around 8.2 V were observed

ity of 50 mA/cm^2, which is suitable for multiplexed display applications.

Both curves in Fig. 2 exhibit the same triangular shape. The straight lines are guides to the eye. Most remarkable is the absolute efficiency maximum at about 3.7 eV, which, to the best of our knowledge, has not been reported so far for pure cathode metals in Alq$_3$-based OLEDs. Thus, for Alq$_3$-based devices, the use of metals with work functions lower than that of magnesium does not result in further device performance enhancement.

Considering onset voltage and operating voltage as a function of the cathode metal work function, a similar effect can be observed (Fig. 3). In the upper part of Fig. 3, the onset voltage difference between the device with the cathode metal under investigation and the Mg reference device are given. Correspondingly, in the lower part of Fig. 3, the driving voltage at a luminance of 1500 cd/m^2 is shown. It is obvious that reducing the work function below the value of magnesium does not reduce onset voltage and operating voltage. Both curves approximate constant straight lines in the low-work-function limit. Usually, the electroluminescence onset was below 3.0 V. For metals with work functions higher than 3.7 eV, onset voltage and operating voltage increase significantly.

3 Discussion

According to [5], holes are the majority charge carriers in OLEDs based on TPD/Alq$_3$. The electron current is limited by the injection from the metal cathode into the electron transporting layer. Then, by adopting the Mott–Schottky relation [13], which is well known from semiconductor physics, the metal–semiconductor transition should become ohmic, when the cathode work function falls below the electron affinity of the adjacent organic material. In our experiments, this should be the case for work functions below or equal to about 3 eV (Yb, Sm, Li, and Ca) [14]. At this point one should mention that direct transfer of semiconductor physics to organic solids may be sophisticated on a molecular scale. However, it is now widely accepted that, basically, the LUMO of an organic solid corresponds to the semiconductor conduction band with respect to charge carrier injection [6–8, 11]. Nevertheless, on a microscopic scale, conduction mechanisms in “classic” inorganic semiconductors are distinct from charge-carrier transport in molecular solids. The latter can be well described by hopping in a particular density of states [15].

In the past, many experiments have been performed to investigate the microscopic mechanism of charge-carrier injection into organic materials [7–9]. Except for magnesium, most of the cathode metals used had a work function lower than the LUMO of the adjacent organic material. In these cases, either thermionic emission [9] or tunneling through a triangular barrier [8] described the injection current fairly well. Arkhipov et al. [7] even took into account the hopping conduction mechanism in amorphous organic materials.

However, in our measurements we observed that onset voltage and operating voltage cannot be decreased continuously by using cathode metals with work functions less than 3.7 eV. Instead, the onset voltage saturates at a value of typically 3.0 V, which is close to the band gap of Alq$_3$ (Fig. 3, upper part). Analogously, the operating voltage at a luminance of 1500 cd/m^2 saturates at 8.2 V (Fig. 3, lower part). Furthermore, the luminous efficiency even slightly decreases for lower work-function metals (Fig. 2). To exclude any impact of the choice of the hole transporting TPD, we reproduced our experimental results presented here by replacing the TPD layer with a bilayer of copper-phthalocyanine and N, N′-bis(naphthalene-1-yl)-N, N′-diphenyl-benzidine (α-NPD). In OLEDs based on the latter layer structure, we obtained the same tendency both for efficiency and onset voltage.

There are several interpretations of the fact that device efficiency cannot be increased by using cathode metals with work functions lower than 3.7 eV (Yb, Sm, Li, Ca). According to Burrows et al. [16, 17], in organic electroluminescent devices based on Alq$_3$ as emitter and Mg cathodes, the electron current is controlled by trap-limited transport in Alq$_3$.

Nevertheless, Matsumura et al. [9] calculated the barrier heights between magnesium and aluminum cathodes and Alq$_3$ by describing the current–voltage characteristics with a thermionic emission model. According to their results, the barrier heights between the cathode metal work functions and the LUMO of Alq$_3$ do not correspond with theoretical values drawn from listed metal work functions. Besides, the observed current densities are much lower than theoretically predicted.

This suggests that chemical changes occur at the metal–organic interface. As already previously reported [14, 18, 19], close to the metal, a chemically modified organic layer is formed, which may extend some distance from the contact. Within this modified layer, transport properties such as mobilities, for example, differ from the bulk material. Different cathodes result in different chemistry, and, therefore, while still being bulk transport (and not injection) limited, devices with very reactive low-work-function cathodes exhibit inferior efficiencies.

The chemical nature of this modified layer might be very complex. Bröms et al. [19] demonstrated the significance of thin oxidic layers on the metal–organic interface. The authors showed that oxidation might even have a positive impact on device performance. Thus, further experiments utilizing ultra-high vacuum conditions will have to shed light on the role of oxidation in our experiments. This might be of significant practical importance with respect to processing conditions in a production line.

One further aspect in this discussion might be diffusion of metal atoms into the Alq_3 layer. In our experiments, we used a variety of cathode metals with very diverse physical and chemical properties, for example, atomic radii or atomic masses. Thus, if we assume diffusion to be a dominating effect, we would not expect devices with Yb (atomic weight 88.9 U) and Li (atomic weight 6.9 U) cathodes to exhibit similar efficiency. However, our measurements clearly indicate that these devices show similar properties (Fig. 3). This argument indicates that diffusion of cathode metal atoms is not a dominating effect, although diffusion may play a role in specific device setups [20].

Charge transfer from cathode metal atoms to electron-transporting Alq_3 molecules is another important aspect that might involve the generation of charge transfer complexes such as “$Mg^+ ... Alq_3^-$”. Ultraviolet photoemission measurements give rise to these assumptions [14, 21]. In these publications, the authors demonstrate the modification of the injection barrier by charge-transfer formation, causing a significant deviation from the expected Mott–Schottky behavior.

4 Summary

We demonstrate the impact of the cathode metal work function on the device performance of organic electroluminescent devices under processing conditions that are relevant for industrial production. Our measurements clearly show that, under high-vacuum processing conditions, low-work-function cathode metals do not automatically improve device performance, but even may deteriorate efficiency. Thus, new electron-injection concepts have to be investigated and optimized further with respect to display application demands. The use of metal alloys [22, 23] or additional thin insulating layers between cathode and electron transport layer as demonstrated by Hung et al. [24] are promising approaches. Temperature-dependent measurements of electron-injecting capabilities would be helpful to clarify the microscopic electrochemical processes occurring during electron injection.

The results presented above are specific for devices with an Alq_3 layer adjacent to the cathode. Nevertheless, as Alq_3 is a widely used electron transport material in OLEDs fabricated from low-molecular-weight materials, our results will have a stimulating impact on application aspects. Packaging issues are clearly an important point of interest, as the use of less reactive cathode metals will obviously reduce the packaging demands of OLED products.

Acknowledgements. The technical help of G. Wittmann, W. Roth, E. Günther, and W. Kurz is gratefully acknowledged. We thank A. Kanitz and J. Schumann for the synthesis of Alq_3 and J. Gudarslu for substrate preparation and technical advice. Part of this work was supported by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF 01 BK 703/4).

References

1. C.W. Tang, S.A. VanSlyke: Appl. Phys. Lett. **51**, 913 (1987)
2. C.W. Tang, S.A. VanSlyke, C.H. Chen: J. Appl. Phys. **65**, 3610 (1989)
3. C. Adachi, T. Tsutsui, S. Saito: Appl. Phys. Lett. **57**, 531 (1990)
4. C. Adachi, S. Tokito, T. Tsutsui, S. Saito: Jpn. J. Appl. Phys., Part 2 **27**, L713 (1988)
5. H. Antoniadis, J.N. Miller, D.M. Roitman: In *Inorganic and Organic Electroluminescence*, ed. by R.H. Mauch, H.-E. Gumlich (Wissenschaft & Technik-Verlag, Berlin 1996)
6. D.V. Khramtchenkov, H. Bässler, V.I. Arkhipov: J. Appl. Phys. **79**, 9283 (1996)
7. V.I. Arkhipov, E.V. Emelianova, Y.H. Tak, H. Bässler: J. Appl. Phys. **84**, 848 (1998)
8. I.D. Parker: J. Appl. Phys. **75**, 1656 (1994)
9. M. Matsumura, T. Akai, M. Saito, T. Kimura: J. Appl. Phys. **79**, 264 (1996)
10. Y. Mori: In *Organic Electroluminescent Materials and Devices*, ed. by S. Miyata, H.S. Nalwa (Gordon and Breach, Amsterdam 1997)
11. Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, K. Imai: Appl. Phys. Lett. **65**, 807 (1994)
12. Y. Sato, S. Ichinosawa, H. Kanai: In *Inorganic and Organic Electroluminescence*, ed. by R.H. Mauch, H.-E. Gumlich (Wissenschaft & Technik-Verlag, Berlin 1996)
13. E.H. Rhoderick, R.H. Williams: *Metal-Semiconductor Contacts*, (Clarendon Press, Oxford 1988)
14. H. Ishii, Kazuhiko Seki: IEEE Trans. Electron Devices **44**, 1295 (1997)
15. For a review see: H. Bässler: Phys. Status Solidi B **175**, 15 (1993)
16. P.E. Burrows, S.R. Forrest: Appl. Phys. Lett. **64**, 2285 (1994)
17. P.E. Burrows, Z. Shen, V. Bulovic, D.M. McCarty, S.R. Forrest, J.A. Cronin, M.E. Thompson: J. Appl. Phys. **79**, 7991 (1996)
18. P. Bröms, J. Birgersson, N. Johansson, M. Löglund, W.R. Salaneck: Synth. Met. **74**, 179 (1995)
19. W.R. Salaneck, S. Strafström, J-L. Brédas: *Conjugated Polymer Surfaces and Interfaces* (Cambridge University Press, Cambridge 1996)
20. V-E. Choong, Y. Park, Y. Gao, T. Wehrmeister, K. Müllen, B.R. Hsieh, C.W. Tang: J. Vac. Sci. Technol. A **15**, 1745 (1997)
21. S.T. Lee, X.Y. Hou, M.G. Mason, C.W. Tang: Appl. Phys. Lett. **72**, 1593 (1998)
22. E.I. Haskal, A. Curioni, P.F. Seidler, W. Andreoni: Appl. Phys. Lett. **71**, 1151 (1997)
23. H. Nakada, T. Tohma: In *Inorganic and Organic Electroluminescence*, ed. by R.H. Mauch, H.-E. Gumlich (Wissenschaft & Technik-Verlag, Berlin 1996)
24. L.S. Hung, C.W. Tang, M.G. Mason: Appl. Phys. Lett. **70**, 152 (1997)
25. S.M. Sze: *Physics of Semiconductor Devices* (Wiley, New York 1981)