

Investigations of molybdenumoxide as the anode-insensitive hole-injection layer

Ting-Yi Cho, Yin-Jui Lu, Chih-Jen Yang, Tung-Huei Ke, Chung-Chih Wu*
 Department of Electrical Engineering, Graduate Institute of Electro-optical Engineering, and Graduate Institute of Electronics Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China
 Phone: +886-2-23635251 ext.346, E-mail: chungwu@cc.ee.ntu.edu.tw

Abstract

In this paper, the thermally evaporated molybdenum oxide (MoO_x) is investigated as the effective hole-injection material for organic light-emitting devices (OLEDs). The use of MoO_x significantly lowers the operating voltage of OLEDs, insensitive to the anode materials used.

1. Introduction

Since OLEDs structure unveiled by Tang *et al* [1] in 1987, extensive investigations on OLEDs have been performed owing to their potential for display and lighting applications. Many efforts have been made to improve the device performance. One critical issue is to reduce the operating voltage by introducing an effective hole-injection layer (HIL) between anode and hole-transport layer (HTL), for increasing the power efficiency [2-6]. The techniques of conductive doping utilizing $\text{F}_4\text{-TCNQ}$ and FeCl_3 have been reported that can reduce the interface barrier and enhance carrier injection. But there are still some stability issues due to smaller molecular weight of these materials. Thus, it is difficult for manipulation and mass production. More recently, transition metal oxides, such as V_2O_5 and WO_3 [4-8], have been reported as well-functional HIL. However, metal oxides such as V_2O_5 and WO_3 are either poisonous (thus not environment friendly) or rather difficult to processing (e.g. very high evaporation temperature etc.).

In this paper, we investigate a thermally evaporated metal oxide layer, molybdenum oxide (MoO_x), as an effective HIL for OLEDs. Devices employed MoO_x layer exhibit lower voltages compared to those utilizing organic hole-injection materials. The operating voltage can be further reduced by replacing the organic transport layer with MoO_x owing to its higher conductivity.

2. Results

The MoO_x film was prepared from high purity MoO_3 powder (>99.99%, Alfa Aesar) by thermal evaporation under high vacuum. Since the melting point of MoO_3 is 930°C , relatively low among metal oxides, the evaporating process is quite stable and feasible to control. Thus, the process of the MoO_x layer is compatible with typical OLEDs manufacturing.

Figure 1 shows the x-ray diffraction pattern of thermally evaporated MoO_x films on quartz substrate. The broad feature indicates an amorphous MoO_x film can be obtained by thermal evaporation. SEM image ($\times 100,000$), shown in the inset of Figure 1, also shows an uniform surface of MoO_x films. According to van der Pauw measurements, neat films of MoO_x exhibit p-type semiconducting characteristics with a resistivity of $\sim 40 \Omega\text{-cm}$, rather small compared with organic materials. Besides, a high transmittance (Figure 2), around 80%, of MoO_x film in visible light region is obtained.

To investigate the effects of the MoO_x layer as a HIL, the device structures **A** and **B**, shown in Figure 3, was tested using various anode materials: Al (with

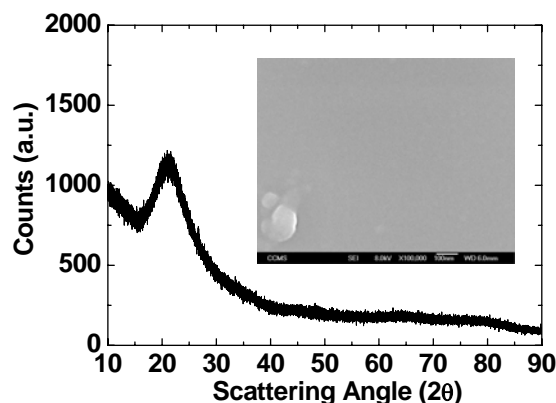


Figure 1. X-ray diffraction pattern of thermally evaporated MoO_x films. Inset: SEM plane view of thermally evaporated MoO_x films.

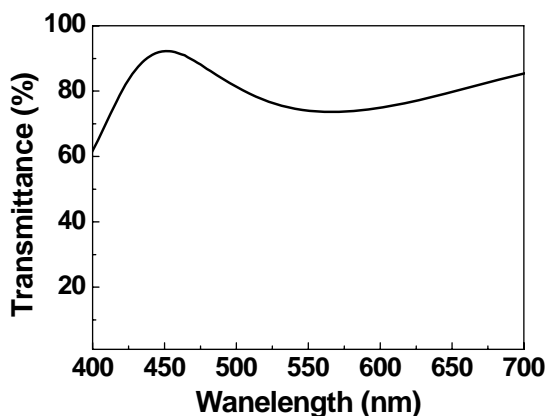


Figure 2. The transmittance spectra of MoO_x films.

work function about 4.1 eV), Ag (4.2 eV), Au (5.1 eV), and ITO (5.0 eV). In this device structure, 45nm $\text{N,N}'$ -Di(naphthalen-1-yl)- $\text{N,N}'$ -diphenylbenzidine (α -NPD), 60nm tris-(8-hydroxyquinoline) aluminum (Alq_3), and LiF/Al were utilized as HTL, electron-transport/emission layer, and cathode, respectively. For the devices without MoO_x (structure A), the operating voltages are very high because of the large energy barrier between the metal and α -NPD. However, by inserting a thin layer of 5nm MoO_x as the HIL between the anode and α -NPD (structure B), the operating voltage drops dramatically compared with that without HIL, as shown in Figure 4. It is notable that with the MoO_x HIL, the voltage drops to quite the same level, regardless of the work functions of the anode materials. According to further studies of the anode/ MoO_x interface by ultraviolet photoelectron spectroscopy (UPS), the vacuum level

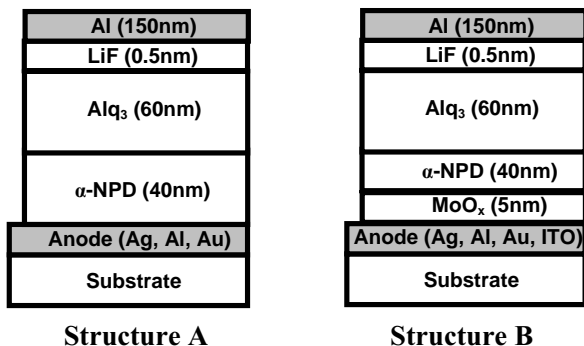


Figure 3. Device architectures A and B of tested OLEDs.

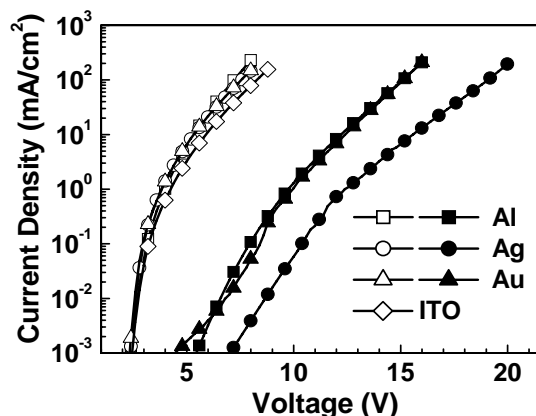


Figure 4. I-V characteristics of devices with various anode materials based on structure A. (open symbols: with 5nm MoO_x as HIL, closed symbols: without HIL)

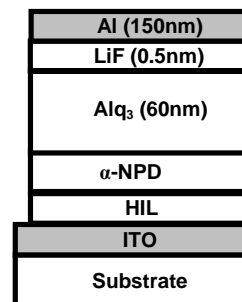


Figure 5. Device architecture C of tested OLEDs.

greatly shifted toward lower energy level at the interface, implying that a localized dipole layer was induced, and thus the injection barrier was reduced.

To explore the use of the higher conductivity of MoO_x for OLEDs, device structure C (Figure 5) with the MoO_x HIL of different thicknesses was fabricated and tested. The layer structures of tested devices are consisted of:

Device a: ITO / m-MTDATA (30nm) / α -NPD (20nm) / Alq_3 (60nm) / LiF (0.5nm) / Al (150nm)

Device b: ITO / MoO_x (5nm) / α -NPD (45nm) / Alq_3 (60nm) / LiF (0.5nm) / Al (150nm)

Device c: ITO / MoO_x (30nm) / α -NPD (20nm) / Alq_3 (60nm) / LiF (0.5nm) / Al (150nm)

Device d: ITO / MoO_x : α -NPD (30nm, vol. 1:4) / α -NPD (20nm) / Alq_3 (60nm) / LiF (0.5nm) / Al (150nm)

Device **a** is the reference device with 4,4',4"-tris(N-3-methylphenyl-N-phenyl-amino)-triphenylamine (m-MTDATA, 30nm) and α -NPD (20nm) as the HIL and the hole-transport layer (HTL), respectively. While for devices **b** and **c** using MoO_x as the HIL, the thicknesses of the HIL (MoO_x) and the HTL (α -NPD) are varied systematically from MoO_x (5nm)/ α -NPD (45nm) in device **b** to MoO_x (30nm)/ α -NPD (20nm) in device **c**. Furthermore a device **d** using the mixed MoO_x : α -NPD (30 nm, vol. 1:4) as the HIL in combination with a HTL α -NPD (s20nm) was also fabricated and tested. Since the conductivity of MoO_x layer is higher than those of organic layers, the operating voltage of devices drops as the thickness of the MoO_x layer increases, as shown in Figure 6(a). Furthermore, by co-evaporating MoO_3 and α -NPD as the composite HIL, the device operating voltage is even lower than the devices **b** and **c**. Since the insertion of MoO_x layer may improve hole injection at ITO/ MoO_x interface, MoO_x / α -NPD interface, and

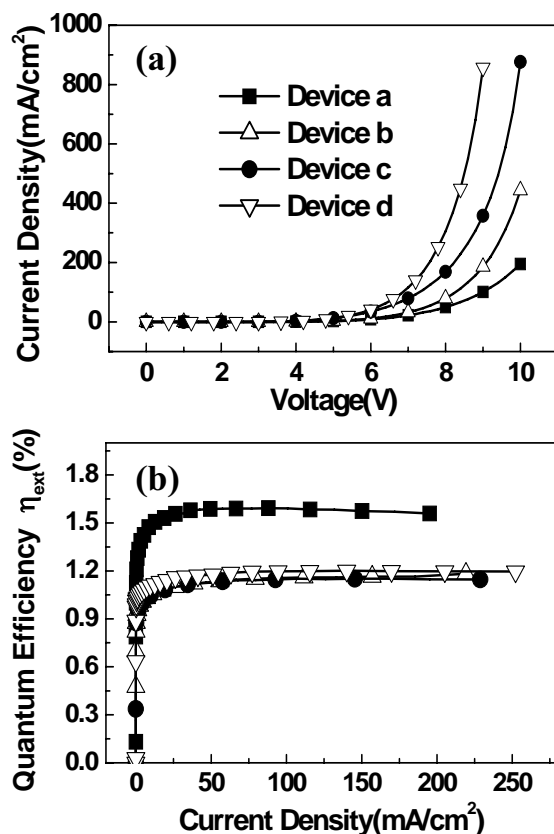


Figure 6. (a) I-V characteristics, and (b) external quantum efficiency of devices with various HIL design based on structure B.

enhance the conductivity in HIL, the composite HIL possesses the best properties among these combined effects. A $>2.5\text{V}$ voltage lowering could be achieved. The devices introducing MoO_3 layer maintain a reasonable external quantum efficiency of 1.2%, shown in Figure 6(b), though lower than reference device. It may be attributed to the carrier imbalance since MoO_x layer greatly enhances hole injection, and may be reduced by improving electron injection (i.e. n-type conductive doping).

While the anode/ MoO_x interface was studied by UPS, it is also useful to know the interaction between the MoO_x and the organic HTL (i.e. α -NPD), since holes injected from MoO_x need to transport from MoO_x to the organic HTL. To get more insights of this interaction, the UV/Vis/NIR absorption spectra of the neat α -NPD, the neat MoO_x and the mixed α -NPD: MoO_x layers were measured and are shown in Figure 7. By mixing α -NPD and MoO_x , new absorption features peaking at 500 nm and 1400 nm are observed. Such features are most probably associated with the charge-transfer states in the composite layer, which would increase the conductivity of the composite layer. Also perhaps the charge-transfer interaction at the interface of the neat α -NPD layer and the neat MoO_x layer largely facilitates hole injection/transport from MoO_x to α -NPD.

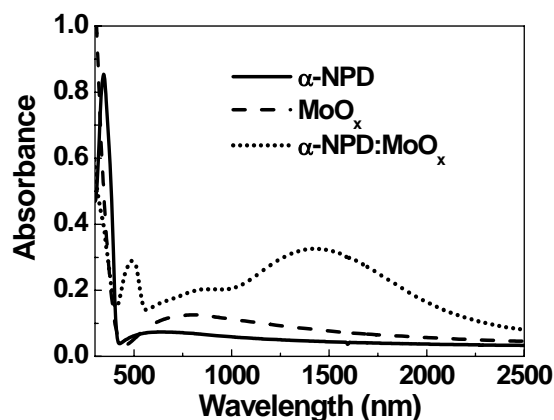


Figure 7. The absorption spectra of the films.

3. Conclusion

We investigated the effective HIL based on thermally evaporated MoO_3 , which is compatible to general processing of OLEDs. The device operating voltage are much reduced and are insensitive to the work function of anode adopted, which feature will be

highly useful for advanced OLEDs such as top-emitting OLEDs and microcavity OLEDs etc. The high conductivity of MoO_x layer also provides an opportunity to achieve high-power-efficiency OLEDs.

4. References

- [1] C.W. Tang, and S.A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
- [2] X. Zhou, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, and K. Leo, *Appl. Phys. Lett.*, **78**, 410 (2001).
- [3] J. Endo, T. Matsumoto, and J. Kido, *Jpn. J. Appl. Phys.*, **41**, L358 (2002).
- [4] S. Tokito, K. Noda, and Y. Taga, *J. Phys. D: Appl. Phys.*, **29**, 2750 (1996).
- [5] J. Li, M. Yahiro, K. Ishida, H. Yamada, and K. Matsushige, *Synth. Met.*, **115**, 141 (2005).
- [6] N. Miyata, T. Suzuki, and R. Ohyama, *Thin Solid Films*, **281-282**, 218 (1996).
- [7] C.-C. Chang, S.-W. Hwang, C. H. Chen, and J.-F. Chen, *Jpn. J. Appl. Phys.*, **43**, 6418 (2004).
- [8] C.-W. Chu, C.-W. Chen, S.-H. Li, E. H.-E. Wu, and Y. Yang, *Appl. Phys. Lett.*, **86**, 253503 (2005).