Chemistry Letters Vol.32, No.2 (2003)

Pronounced Effect of the Methods of Preparation of Organic Thin Films on Hole Injection from the Indium-tin-oxide Electrode–Vacuum Deposition vs Spin Coating

Mari Ishihara, Kenji Okumoto, and Yasuhiko Shirota*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871

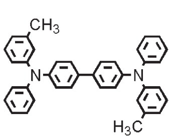
(Received October 18, 2002; CL-020891)

The methods of preparation of organic thin films of hole-transporting materials, vacuum deposition and spin coating, were found to exert a pronounced influence on charge injection from electrodes into organic layers in organic electroluminescent devices, depending upon the kind of hole transporters.

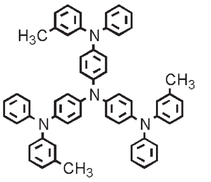
Organic thin films are a subject of current interest and have been widely investigated for use in electronic, optoelectronic and photonic devices. For organic electroluminescent (EL) devices, the control of the interface between the electrode and the organic layer is of crucial importance for achieving efficient charge injection and hence high performance of devices.

Thin films of 4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenylamine (*m*-MTDATA) and copper phthalocyanine have been used as a buffer layer to facilitate hole injection from an indium-tin-oxide (ITO) electrode into an adjacent hole-transport layer or an emitting layer with hole-transporting properties in organic EL devices.[1,2] The adsorption of polar molecules, e.g., phosphoric acid and phosphonic acid derivatives, on the surface of the ITO electrode has also been reported to enhance hole injection from the ITO electrode into hole-transporting materials, reducing drive voltage in organic EL devices.[3,4]

Usually, thin films of small organic molecules have been prepared by vacuum deposition; however, small organic molecules that readily form amorphous glasses, i.e., amorphous molecular materials, also form uniform amorphous thin films by spin coating from solution.[5] We report here a pronounced effect of the methods of preparation of organic thin films of hole-transporting amorphous molecular materials, vacuum deposition and spin coating, on charge injection from electrodes into organic layers in organic EL devices. It depends upon the kind of hole transporters; *N,N*′-bis(3-methylphenyl)-*N,N*′-diphenyl-[1,1′-biphenyl]-4,4′-diamine (TPD) and *m*-MTDATA contrast with each other.



TPD



m-MTDATA

Organic EL devices were fabricated using TPD and *m*-MTDATA as hole transporters and tris(quinolin-8-olato)aluminium (Alq_3) as an emitter, sandwiched between the ITO and an alloy of magnesium and silver electrodes. The ITO electrode (ca. 50 Ω sq.$^{-1}$, Geomatec) was cleaned by being immersed in an ultrasonic bath of 1,1,1-trichloroethane, followed by exposure to hot acetone vapor and UV ozone immediately before use. Thin films of the above hole transporters were prepared on an unheated, cleaned ITO-coated glass substrate by vacuum deposition or spin coating. Vacuum deposition was carried out at a deposition rate of 2–3 Å s^{-1} at 10^{-5} Torr. Spin coating was carried out with freshly distilled THF solution of the hole transporters at a spinning rate of 3000 rpm at room temperature, followed by immediate vacuum drying for 1 h at 10^{-5} Torr to evaporate any residual solvent. Then, a thin film of Alq_3 was vacuum deposited onto the hole-transport layer at a deposition rate of 2–3 Å s^{-1} at 10^{-5} Torr, followed by vacuum deposition of an alloy of magnesium and silver (atomic ratio 10:1) by simultaneous evaporation from two separated sources. Both vacuum-deposited and spin-coated films of TPD and *m*-MTDATA were amorphous, as confirmed by X-ray diffraction and polarizing microscopy.

It was found that the methods of preparation of the films of the hole-transporting amorphous molecular materials greatly affect the injected current density and hence the performance of organic EL devices. As Figure 1(a) shows, the bilayer organic EL device consisting of the spin-coated film of TPD as the hole-transport layer and Alq_3 as the emitting layer, ITO/TPD(700 Å)/Alq_3(300 Å)/MgAg, showed a ten-fold greater injected current density at applied voltages below 7 V than the corresponding device using the vacuum-deposited TPD. The observed one-order greater injected current density is not due to a leak current. The magnitude of a current observed for these devices by reversing the polarity of applied voltage, namely, by applying the positive voltage to the MgAg electrode, was almost the same irrespective of the difference in the methods of the preparation of thin films, being approximately one hundredth of the injected current observed for the device using the vacuum-deposited TPD. These results indicate that strikingly enhanced hole injection from the ITO electrode into the hole-transport layer of TPD took place for the device using its spin-coated film relative to the device using the vacuum-deposited film.

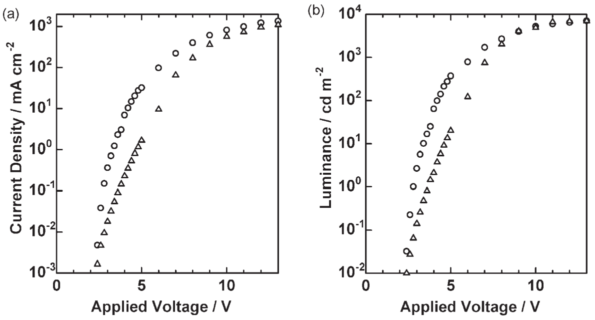


Figure 1. (a) Injected current density–applied voltage and (b) luminance–applied voltage characteristics of organic EL devices using TPD as a hole-transport layer, ITO/TPD(700 Å)/Alq_3(300 Å)/MgAg; vacuum-deposited TPD film (triangle) and spin-coated TPD film (circle).

As is evident from Figure 1(b), the device using the spin-coated film of TPD also exhibited approximately ten-fold higher luminance at applied voltages below 7 V than the device using the vacuum-deposited film of TPD. The device using the spin-coated TPD film resulted in the reduction of drive voltage relative to the device using the vacuum-deposited TPD. That is, the turn-on voltage for obtaining a luminance of 1 cd m^{-2} were 3.7 and 2.8 V, and the voltage for obtaining a luminance of 300 cd m^{-2} were 6.2–6.9 and 5.0–5.4 V for the devices fabricated with the vacuum-deposited and spin-coated TPD, respectively. The external quantum efficiency of EL (Φ_{EL}) was almost the same for both devices using the vacuum-deposited and spin-coated films of TPD (Φ_{EL} at a luminance of 300 cd m^{-2} : 0.36–0.40% and 0.31–0.37% for the devices using vacuum-deposited and spin-coated TPD) because of the almost equivalent increase of both the injected current density and the luminance. The improved luminance characteristics for the device using the spin-coated TPD indicate the increase in the number of recombined charge carriers. This means that electron injection from the cathode into the Alq$_3$ layer is also facilitated in the device using the spin-coated film of TPD as the hole transporter. It is thought that hole carriers are more accumulated at the interface between the spin-coated TPD and Alq$_3$ layers because of enhanced hole injection, and hence a steeper electric field is applied in the Alq$_3$ layer to lead to enhanced electron injection.

By contrast, almost no difference was observed in the luminance–applied voltage–current density characteristics between the organic EL devices fabricated with vacuum-deposited and spin-coated films of *m*-MTDATA as a hole-injection layer and the vacuum-deposited thin film of TPD as a hole-transport layer, ITO/*m*-MTDATA(600 Å)/TPD(100 Å)/Alq$_3$(300 Å)/MgAg. The turn-on voltages for obtaining a luminance of 1 cd m^{-2} were 2.7 V and the voltages for obtaining a luminance of 300 cd m^{-2} were ca. 5.0 V for both devices. Thus, the hole injection behavior from the ITO electrode into the *m*-MTDATA layer is independent of the methods of preparation of the film.

Similar behavior as observed for TPD and *m*-MTDATA, respectively, was also observed for other materials, *N,N′*-di(biphenyl-4-yl)-*N,N′*-diphenyl-[1,1′-biphenyl]-4,4′-diamine[6] and 4,4′,4″-tris[2-naphthyl(phenyl)amino]triphenylamine,[7] respectively.

In order to gain information on the origin of enhanced hole injection for the spin-coated TPD film relative to its vacuum-deposited film and the origin of the absence of such behavior with *m*-MTDATA, we have observed atomic force microscopy (AFM) images of the surface of the vacuum-deposited and spin-coated thin films (film thickness : 150 Å) of TPD and *m*-MTDATA prepared on the ITO electrode. The surface of the ITO electrode is not flat but rough, exhibiting surface features with a mean surface roughness (Ra) of ca. 30 Å (Figure 2(a)). The AFM images of both the vacuum-deposited and spin-coated *m*-MTDATA films (Figure 2(b) and (c)) resemble that of the ITO electrode, showing the similar surface features. On the other hand, the AFM images of the vacuum-deposited and spin-coated films of TPD are different from each other (Figure 2(d) and (e)). The spin-coated film of TPD shows surface features more or less similar to those of the ITO electrode; however, the vacuum-deposited TPD film shows different features. It is suggested that both the vacuum-deposited and spin-coated films of *m*-MTDATA and the spin-coated film of TPD are formed along the surface features of the ITO electrode. These results imply that the features of the contact between the ITO electrode and the TPD layer, e.g., contact area, may be different depending upon the methods of the preparation of films, which is responsible for the remarkable difference in the hole injection behavior between the devices using the vacuum-deposited and spin-coated films of TPD.

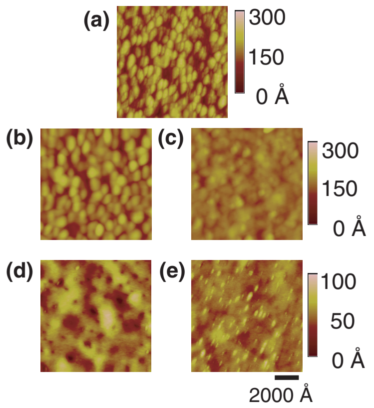


Figure 2. AFM images (1 µm × 1 µm) of cleaned ITO electrode and *m*-MTDATA and TPD thin films with a thickness of 150 Å prepared on the ITO electrode: (a) ITO electrode, (b) vacuum-deposited *m*-MTDATA, (c) spin-coated *m*-MTDATA, (d) vacuum-deposited TPD, and (e) spin-coated TPD.

The present study has demonstrated for the first time a striking effect of the methods of preparation of organic thin films of hole-transporting amorphous molecular materials on charge injection from electrodes in organic EL devices, providing new insight into the control of the interface between the electrode and the organic layer in electronic and optoelectronic devices.

References

1 Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, and K. Imai, *Appl. Phys. Lett.*, **65**, 807 (1994).
2 S. A. Van Slyke, C. H. Chen, and C. W. Tang, *Appl. Phys. Lett.*, **69**, 2160 (1996).
3 F. Nuesch, E. W. Forsythe, Q. T. Le, Y. Gao, and L. J. Rothberg, *J. Appl. Phys.*, **87**, 7973 (2000).
4 S. F. J. Appleyard, S. R. Day, R. D. Pickford, and M. R. Willis, *J. Mater. Chem.*, **10**, 169 (2000).
5 Y. Shirota, *J. Mater. Chem.*, **10**, 1 (2000).
6 Y. Shirota, K. Okumoto, and H. Inada, *Synth. Met.*, **111–112**, 387 (2000).
7 Y. Shirota, Y. Kuwabara, D. Okuda, R. Okuda, H. Ogawa, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, and K. Imai, *J. Lumin.*, **72–74**, 985 (1997).