

# Pulsed laser deposition of organic thin films

L.D. Wang, H.S. Kwok\*

Department of Electrical Engineering, Hong Kong University of Science & Technology, Clear Water Bay, Hong Kong

## Abstract

Excimer laser pulsed deposition was applied to the deposition of organic thin films on sapphire and on glass. The thin films were analyzed by X-ray diffraction (XRD), micro-Raman spectroscopy and ESCA. It was found that the properties of the films were very close to that of the target materials. Strong photoluminescence was observed for both Alq<sub>3</sub> and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD), indicating that laser deposition is a viable method for the deposition of these organic materials. An interesting increase in the photoluminescent (PL) signal of Alq<sub>3</sub>/GaP multi-layers was observed. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Pulsed laser deposition; Organic thin films; Photoluminescent

## 1. Introduction

Electroluminescence (EL) has been observed in small organic molecules as well as polymers [1–6]. These discoveries are having tremendous impact on the field of information display and opto-electronics. For the case of small molecules, the thin films needed in the electroluminescent devices are mostly deposited by thermal evaporation [2–5]. For the case of polymers, spin coating is employed.

Since the performance of any thin film device should depend strongly on the quality of the thin films, it is important to explore the use of other deposition techniques in optimizing the properties of the organic thin films. Recently, ion-assisted deposition (IAD) has been attempted where luminescent devices with higher lumens per watt than thermally evaporated ones were made [6]. Pulsed laser deposition (PLD) with KrF laser has also been applied to deposit copper phthalocyanine (CuPC) and the result was found to be satisfactory [7].

PLD is an excellent thin film technique that has been applied to the deposition of many kinds of materials including many semiconductors, insulating as well as conducting metal oxides [8]. It should be explored further to see if better EL devices can be obtained. We recently found that PLD could be used to deposit reasonably good quality *Tris*-(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>) [9]. In this paper, we wish to show that PLD can also be used for the deposition of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) thin films. In addition, we shall

report an interesting increase in photoluminescent signals using laser deposited multi-layers of Alq<sub>3</sub> and GaP.

## 2. Experimental

For PLD, it is important to verify that the molecular structure as well as the luminescent properties of these important organic materials can be preserved during laser deposition. The experiment was performed in a standard vacuum deposition chamber with a base pressure of 10<sup>-5</sup> Torr. An ArF excimer laser at 193 nm was used.

Pressed pellets of Alq<sub>3</sub> and TPD were used as the targets. For GaP deposition, a GaP wafer was used. The laser was rastered on the target in order to avoid deterioration. For TPD deposition, Al<sub>2</sub>O<sub>3</sub>(0001) was used as the substrate. The chamber was filled with 20 mTorr of nitrogen during deposition. The action of the background gas was to slow down the laser plume and avoid formation of energetic atomic and ionic species [8]. The substrate was kept at room temperature during deposition.

The laser fluence is an important parameter in the deposition of the organic films. For traditional PLD of inorganic materials, a fluence of ~2 J/cm<sup>2</sup> is used typically. It was found that in the case of organic films, fluences higher than 0.9 J/cm<sup>2</sup> will produce blackened films, indicating a decomposition of the target. At lower fluences, clear films are obtained. The deposition rate was measured with an alpha step profilometer. It is measured as a function of the laser pulse fluence. Fig. 1 shows the experimental results obtained for the case of Alq<sub>3</sub>. It is seen that the threshold for laser deposition is about 0.062 J/cm<sup>2</sup>. Above the threshold, the deposition rate is quite linear. Thus, it can be seen

\* Corresponding author. Tel.: + 852-2358-7056; fax: + 852-2358-1485.

E-mail address: eewok@usthk.ust.hk (H.S. Kwok)

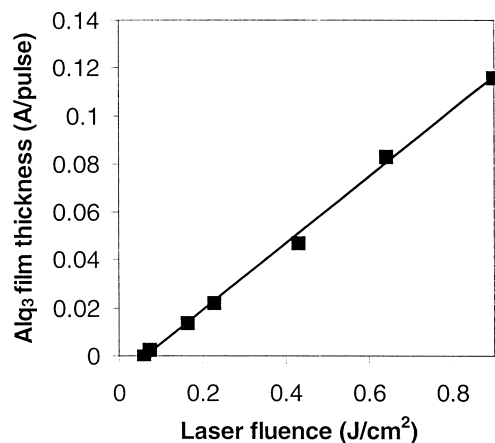


Fig. 1. Deposition rate of Alq<sub>3</sub> as a function of laser fluence.

that the window for the deposition of organic films is quite large. This result is also in contrast to the earlier results of Ina et al. [7] where they used a low fluence of 30 mJ/cm<sup>2</sup>. It may be due to the difference KrF laser and the ArF laser wavelengths.

Films deposited at 0.65 J/cm were further used for characterization. At this fluence, the deposition rate is about 10 pm/pulse. The sample used was a 180-nm thin film. Micro-Raman spectroscopy, ESCA, XRD (X-ray diffraction), and photoluminescence were used. In a previous publication, the results for Alq<sub>3</sub> were shown, indicating that the film obtained was indeed very similar to that of the target. Figs. 2–4 show similar results for case of TPD. Fig. 2 shows the ESCA spectra of the target as compared to that of the film. It can be seen that the chemical bond strengths of the film and the target are about the same, with perhaps a slight blueshift of the peaks for the films.

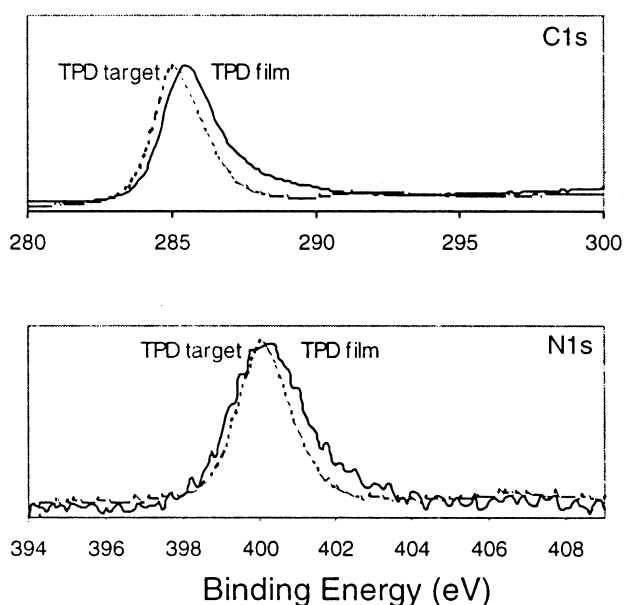


Fig. 2. ESCA spectra of TPD target and TPD thin films.

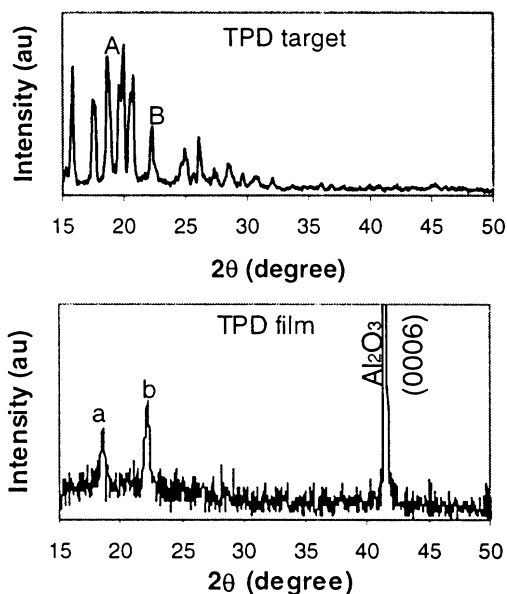


Fig. 3. XRD spectra of the TPD target (upper curve) and the TPD thin film (lower curve). Vertical scale is arbitrary.

### 3. Results and discussion

Fig. 3 shows the XRD spectra of the target and the TPD thin film. A few of the crystalline peaks in the target are reproduced in the thin film, indicating some crystallinity of the TPD film. The reduction in the number of diffraction peaks is perhaps indicative of the better alignment of the polycrystals to the substrate.

Fig. 4 shows the photoluminescence spectra of the target and the thin film. A 325-nm He–Cd laser was used for the PL measurement. Very strong blue PL was observed in both cases. The spectra are similar in shape, with the film showing a 5-nm blueshift. These results are very similar to the case of Alq<sub>3</sub>. The blueshift of the PL, the Raman peak and the ESCA peaks indicate that the molecules in the PLD films are highly stressed. This is perhaps due to the rapid

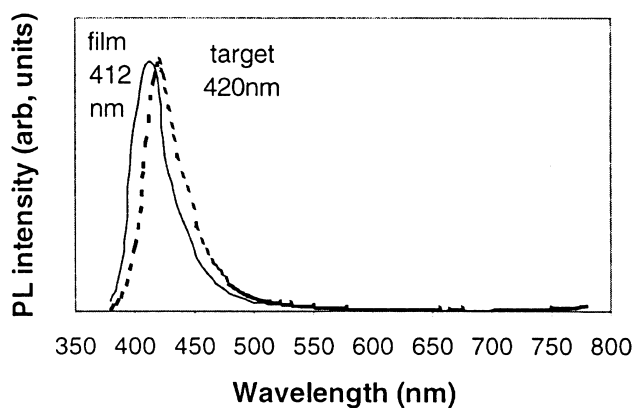


Fig. 4. PL spectra of the TPD thin film (lower curve) and the target (upper curve). Vertical scale is arbitrary.

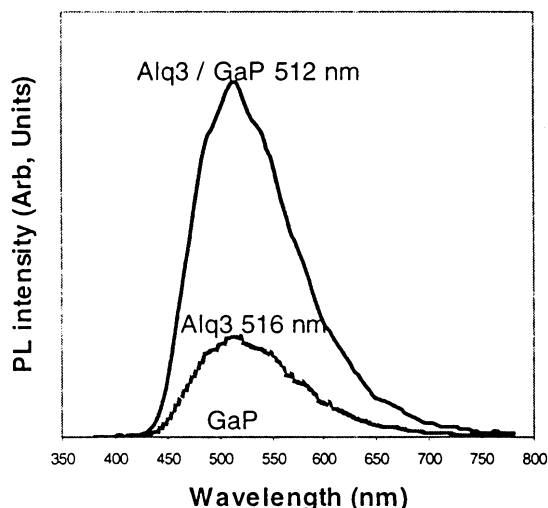


Fig. 5. Relative PL spectra of pure GaP film, pure Alq<sub>3</sub> film and Alq<sub>3</sub>/GaP multi-layer film.

deposition rate in PLD, and insufficient relaxation due to the low deposition temperature. Perhaps post-deposition annealing can reduce such stress.

Thus, PLD is a viable technique for the deposition of organic thin films. It is believed that the deposition mechanism is that of evaporation of the molecules instead of evaporation of atoms as in conventional PLD of inorganic films. The molecules are transported in free space to the substrate. This is evidenced by the strong luminescence from the laser-generated plumes that emit strongly at exactly the same wavelengths as the target. Due to the rapid ablation of the molecules, they possess quite a bit of momentum and kinetic energies.

The major advantage of PLD is that it is a versatile technique, which can be applied to many different materials. Thus, it is possible to deposit organic films together with inorganic films and for multi-layer structures. We made such an initial attempt by depositing Alq<sub>3</sub> and GaP multi-layers. The experimental procedure is as follows: we first deposit a 15-nm thick Alq<sub>3</sub> on ITO glass. We then repeat the same deposition with alternating Alq<sub>3</sub> and GaP films of 2 nm thick each. The substrate temperature was at room temperature while the ambient pressure was 0.02 Torr of N<sub>2</sub>.

The deposition rates of Alq<sub>3</sub> and GaP were calibrated carefully first. The fluence for Alq<sub>3</sub> deposition was 0.64 J/cm<sup>2</sup>, while that for GaP deposition was 2.86 J/cm<sup>2</sup>. At these fluences, the deposition rate of Alq<sub>3</sub> was about  $8.3 \times 10^{-3}$  nm/pulse, while it was  $23.6 \times 10^{-3}$  nm/pulse for GaP. Six periods of 24-nm each of Alq<sub>3</sub> and GaP were deposited. The expected total thickness was 288 nm and the measured

thickness was 305 nm. Therefore, the error in thickness calibration was less than 6%.

Thus, the total thickness of Alq<sub>3</sub> in the pure Alq<sub>3</sub> sample and the multilayer sample are about the same. Fig. 5 shows the PL spectra of the pure Alq<sub>3</sub> sample, the Alq<sub>3</sub>/GaP multi-layer and a pure GaP sample. It can be seen that the pure GaP sample shows no PL signal, while the multi-layer shows a  $\times 3$  increase in PL signal vs. the pure Alq<sub>3</sub> sample.

The increase in the PL signal for the multi-layer is very interesting. It points to the possibility of increasing the efficiency of electroluminescent devices. At present, we do not have a good explanation to the increased signals. It may have to do with the confinement effect of the Alq<sub>3</sub> by the wide bandgap GaP. Or it may simply be that the multi-layered films have a better crystalline structure for PL.

#### 4. Conclusions

In summary, we have successfully deposited TPD films on Al<sub>2</sub>O<sub>3</sub>(0001) using the method of pulsed laser deposition. Good quality thin films have been produced, with good PL properties. We have also observed an interesting increase in PL signals for a multi-layer film of Alq<sub>3</sub> and GaP on glass. Such organic/semiconducting thin films can be formed easily with the pulsed laser deposition method. It points to the potentially interesting prospect of combining organic and inorganic materials in EL devices.

#### Acknowledgements

This research was supported by a grant from the Research Grants Council of the Hong Kong SAR Government.

#### References

- [1] C.W. Tang, S.A. Vanslyke, *Appl. Phys. Lett.* 51 (1987) 913.
- [2] G. Gu, P.E. Burrows, S. Vankatesh, S.R. Forrest, M.E. Thompson, *Opt. Lett.* 22 (1997) 172.
- [3] V.E. Chong, Y. Park, Y. Gao, M.G. Mason, C.W. Tang, *J. Vac. Sci. Technol. A* 16 (1998) 1838.
- [4] T. Mori, K. Obata, K. Miyachi, T. Mizutani, Y. Kawakami, *Jpn. J. Appl. Phys.* 36 (1997) 7239.
- [5] S.T. Lee, X.Y. Hou, M.G. Mason, C.W. Tang, *Appl. Phys. Lett.* 72 (1998) 1593.
- [6] H. Usui, K. Tanaka, H. Orito, S. Sugiyama, *Jpn. J. Appl. Phys.* 37 (1998) 987.
- [7] E. Ina, N. Matsumoto, E. Shikada, F. Kanari, COLA '97, Monterey, CA, 1997.
- [8] R.F. Xiao, X.W. Sun, Z.F. Li, N. Cue, H.S. Kwok, Q.Z. Liu, S.S. Lau, *Vac. Sci. Technol. A* 15 (1997) 2207.
- [9] L.D. Wang, H.S. Kwok, (1999) in press.