

## Studies of mist deposition in the fabrication of blue organic light emitting diodes

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2008 Semicond. Sci. Technol. 23 075036

(<http://iopscience.iop.org/0268-1242/23/7/075036>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 128.6.218.72

This content was downloaded on 20/08/2015 at 14:54

Please note that [terms and conditions apply](#).

# Studies of mist deposition in the fabrication of blue organic light emitting diodes

K Shanmugasundaram<sup>1</sup>, S C Price<sup>1</sup>, W Li<sup>2</sup>, H Jiang<sup>2</sup>, J Huang<sup>2</sup>,  
Q K Wang<sup>2</sup>, Y Yang<sup>3</sup> and J Ruzyllo<sup>1</sup>

<sup>1</sup> Department of Electrical Engineering, The Pennsylvania State University, 11 Electrical Engineering West, University Park, PA 16802, USA

<sup>2</sup> Agiltron Inc., 15 Cabot Rd, Woburn, MA 01801, USA

<sup>3</sup> Department of Materials Science and Engineering, University of California, Los Angeles, CA, USA

E-mail: [kxs423@psu.edu](mailto:kxs423@psu.edu)

Received 24 February 2008, in final form 2 April 2008

Published 28 May 2008

Online at [stacks.iop.org/SST/23/075036](http://stacks.iop.org/SST/23/075036)

## Abstract

In this work, the process of mist deposition is explored as a method used to deposit organic semiconductors for applications in organic light emitting diodes (OLEDs). The deposition kinetics of a specially formulated hole transport agent is studied. The results indicate that the mist-deposited organic film thickness varies linearly with precursor concentration, deposition time and substrate potential. Depending upon process parameters, a deposition rate in the range of 50 nm min<sup>-1</sup> is readily achievable. Evolution of surface roughness revealed distinct stages in the film formation process. The growth of secondary layers was observed before the formation of a complete initial film layer. A working OLED with the hole transport layer deposited by mist deposition was demonstrated. The luminance of the device was measured to be a maximum of 3000 cd m<sup>-2</sup> and the efficiency was 6.7 cd A<sup>-1</sup>.

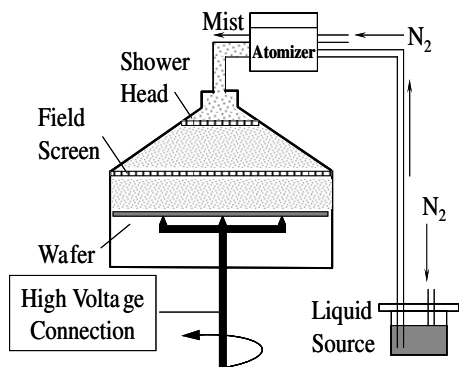
## 1. Introduction

Recently, organic semiconductor thin film devices, including organic light emitting diodes (OLEDs) [1–3] and organic thin film transistors (OTFTs) [4, 5], have been extensively studied for potential applications in display technology. Several reports have introduced working OLEDs and OTFTs fabricated from solution-processed organic thin films (e.g. [6, 7]). The performance of these devices has improved over the years to be comparable to organic semiconductor devices fabricated by vacuum processing technologies.

Several techniques including spin coating and dip casting have been reported for the deposition of organic semiconductor thin films from liquid precursors [8, 9]. However, these methods may not be able to provide adequate control of film thickness, surface morphology and patternability for efficient devices for the manufacture of large displays. These limitations warrant the continued exploration of alternate technologies in the deposition of thin films for applications in organic displays. Mist deposition is one such technique that has been demonstrated with good results in a number

of applications including high-*k* dielectrics, photoresist, ferroelectric materials and nanocrystal quantum dots [10–12]. In this process, the liquid precursor is converted into a very fine mist which is then carried by nitrogen to the deposition chamber where submicron droplets coalesce at room temperature into the substrate covering its surface with a uniform film of viscous liquid which is then solidified using low-temperature thermal curing. Details of the process are discussed elsewhere (e.g. [11]). Mist deposition offers advantages over other physical liquid deposition methods in that it allows selective deposition [13] and patterning of deposited materials, eliminating the need for post-deposition lithography and etches. At the same time it does not differ from other solution processing methods, from neither the point of view of thermal, budget required nor type of solvents used.

In this experiment, mist deposition is for the first time employed in the formation of thin organic semiconductor films in the fabrication of blue light emitting diodes. The kinetics of the film deposition process is investigated and feasibility of OLED formation using mist deposition of solution-processed organic semiconductors is explored.



**Figure 1.** Schematic of the mist deposition system used in this study.

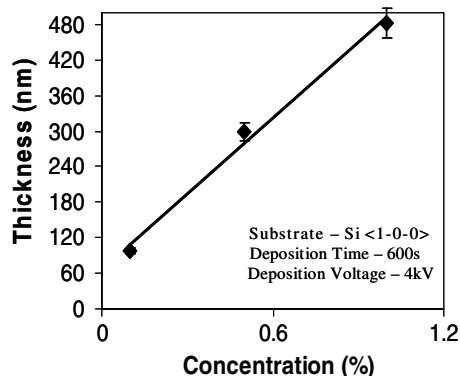
## 2. Experimental details

The principle of mist deposition is to convert the liquid source material into a fine mist of submicrometer size droplets, which is then carried in a pressurized stream of  $N_2$  gas into the deposition chamber (figure 1) where the droplets are allowed to coalesce into the substrate at room temperature at atmospheric pressure. This process forms a uniform film of liquid on the substrate, which is then thermally treated to burn off the solvent and leave a thin film of solid on the surface.

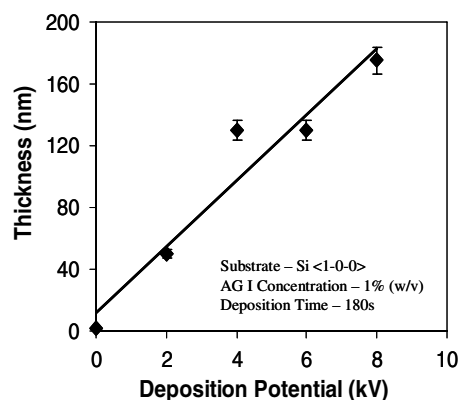
In order to control the deposition rate beyond gravitational interactions, which in the case of submicrometer-sized droplets are very weak, an electric field is created between the grounded field screen and a wafer (figure 1). After deposition, the film is thermally cured at the temperature of 100–300 °C in ambient air or in the controlled ambient of either  $O_2$  or  $N_2$  at the atmospheric pressure.

The polymeric material used in this study is a hole transport agent with potential uses in organic light emitting devices and solar cells. It is a proprietary hole transport agent (AG I) provided by Agiltron, Inc. Three different concentrations of AG I in a toluene solvent were studied: 0.1% (w/v), 0.5% (w/v) and 1% (w/v). The deposited films were subjected to a hot-plate anneal in ambient air at 100 °C for 2 min to drive off the excess solvent. The OLEDs processed in this experiment were ITO/AG I/PFO/Al structures in which an active layer comprising 1% wt AG I was mist deposited and a poly(9, 9-dioctylfluorene) (PFO) layer spin coated. In the working diodes, the thickness of AG I was estimated to be 200 nm and the PFO thickness was estimated to be between 80 and 100 nm. Al contacts were then vacuum evaporated through a shadow mask to define a 12 mm<sup>2</sup> electrode area.

The films were deposited on two different substrates: Si and ITO-coated glass. The substrates were prepared as follows prior to deposition. Si substrates were subjected to a standard RCA1 (6:1.5:1 DI  $H_2O$ : $H_2O_2$ : $NH_4OH$ ) clean [14] for 10 min at 80 °C followed by etch off in a 1:100 HF:DI  $H_2O$  solution unless otherwise noted. The ITO-coated glass substrates were subjected to a solvent clean in acetone followed by IPA rinse. The remaining organics were burned off by a lamp clean at 300 °C for 1 min [15]. Any other treatments that were performed will be described accordingly. Deposited



**Figure 2.** Thickness versus precursor concentration of a polymeric film (AG I) on Si substrates.



**Figure 3.** Thickness versus deposition potential of a polymeric film (AG I) on Si substrates.

films were characterized by AFM analysis and spectroscopic ellipsometry after thermal curing as described earlier. The OLEDs formed were measured using a computer-controlled source meter equipped with a calibrated silicon photodetector.

## 3. Results and discussions

The deposition kinetics of the AG I films deposited on Si substrates was studied first. Figure 2 shows the dependence of material concentration on the thickness. Films in this case were deposited at 4 kV for 600 s starting with precursors of three different concentrations. It is seen from figure 2 that thickness increases linearly with concentration, which is expected. The thickness for the 0.1% concentration precursor is 97.5 nm and that for the 1% concentration solution is 482 nm. The difference in the film thickness is explained by the change in viscosity of the solution with material concentration. Kim and Marshall showed that the droplet size of a liquid increases with the viscosity of the solution [16]:

$$D \sim (\eta/\rho\sigma)^{0.45},$$

where  $D$  is the mean droplet diameter,  $\eta$  is the viscosity of the liquid,  $\rho$  is the density of the liquid and  $\sigma$  is the surface tension. As the material concentration increases, the diameter of the mist droplets also increases thereby depositing a larger volume

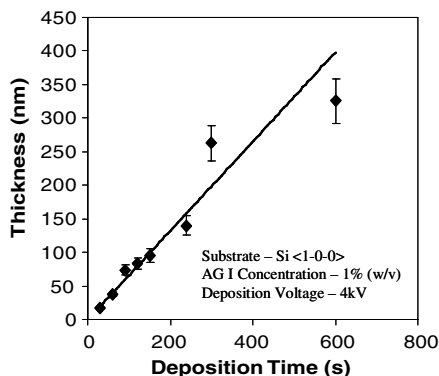


Figure 4. Thickness versus deposition time of a polymeric film (AG I) on Si substrates.

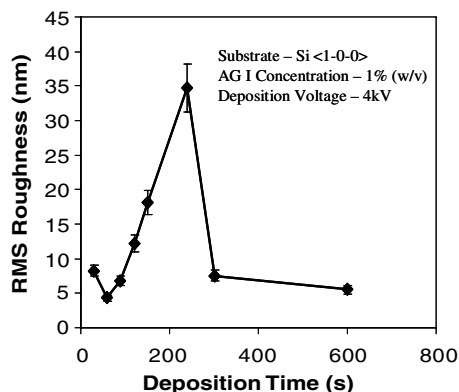


Figure 5. RMS roughness versus deposition time of a polymeric film (AG I) on Si substrates.

of a liquid film on the substrate which when thermally annealed leaves more material on the surface. This relationship was

confirmed by Chang *et al* [17] in the case of mist deposition of HfSiO<sub>4</sub> precursors.

The thickness versus the substrate potential relationship for 3 min depositions is shown in figure 3. As seen, the increase in thickness with the mist deposition time is linear. The flattening of the growth rate between the 4 kV and 6 kV substrates is possibly due to nonlinearity in the film formation. This might be due to the growth of secondary and tertiary layers before the first layers are completely formed. As the potential increases, there is no growth in thickness but the deposited material is used to fill the voids created by the early growth of the secondary layers. This phenomenon is discussed further in the subsequent sections.

Figure 4 shows the increase in film thickness with the deposition time. All films were deposited with a precursor concentration of 1% w/v in toluene, at a substrate potential of 4 kV. It is seen from figure 4 that the thickness increases almost linearly with the deposition time. This is typical of most materials deposited by mist deposition. It is to be noted that the initiation time for the film growth is very short in this case, and there is a complete film with a thickness of about 26 nm in the first 30 s of deposition.

The RMS roughness data in figure 5 indicate that as the deposition time increases the roughness increases and then decreases abruptly, again indicating the possible formation of secondary film layers before the formation of complete initial layers. The roughness after a 30 s deposition is 8.2 nm which then decreases to 4.5 nm after 60 s of deposition, thereby confirming the formation of an initial film layer. The roughness then increases to about 47.1 nm for a 240 s deposition after which it decreases to 7.5 nm after 300 s. This is believed to mark the growth of a complete film layer. It is also important to note that the difference in thickness between the complete formation of the first layer and the second layer

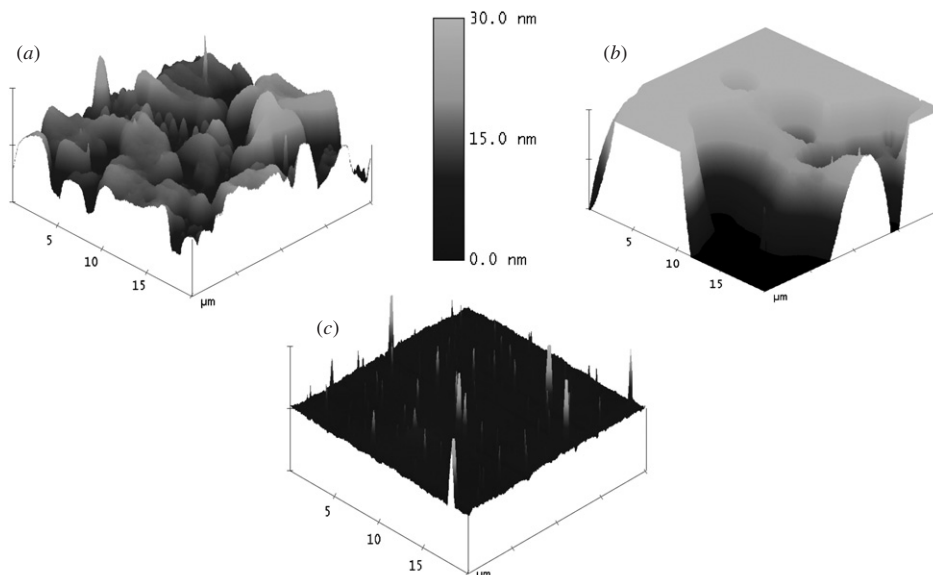
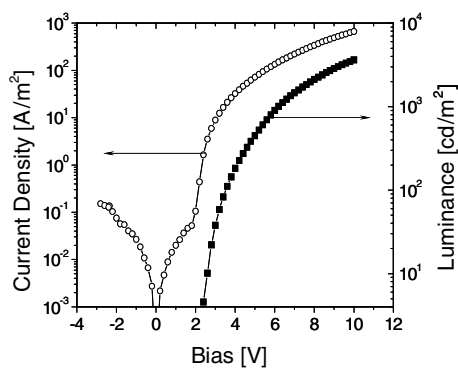


Figure 6. AFM images of a polymeric film (AG I) on Si substrates for three deposition: (a) 30 s, (b) 240 s, and (c) 300 s.



**Figure 7.** Luminance and current density versus applied bias of a mist-deposited OLED.

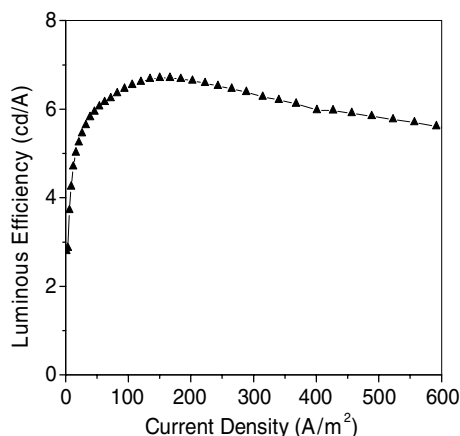
is significantly larger compared to the thickness of the initial layer. This shows that there is a layer-by-layer growth mode on the Si substrate immediately prior to the formation of the initial polymer layer. The growth of the secondary layer proceeds with island formation with the growth of multiple layers before the islands coalesce to form a complete layer.

Atomic force microscope images of the deposited films at 60, 240 and 300 s are shown in figures 6(a)–(c), respectively. These images clearly show the distinct stages in the growth of the AG I layer with the growth of secondary layers before the initial layer is complete. The spikes seen on these images are large enough to be considered as the growing film. It is postulated that the additional material deposited during the longer deposition times is used in filling the voids created by the earlier layers and does not contribute to a significant increase in film thickness.

In the last part of this experiment, the ITO/AG I/PFO/Al OLEDs in which an active layer comprised mist deposited 1% wt AG I were processed. The measured luminance and current density versus voltage characteristics of the fabricated OLEDs are shown in figure 7. It is seen from this figure that the diode has a maximum luminance of  $3000 \text{ cd m}^{-2}$  at 10 V, and the turn-on voltage is 2.3 V. Figure 8 shows the electroluminescence efficiency versus current density. The efficiency reaches a maximum of  $6.7 \text{ cd A}^{-1}$  at a current density of  $150 \text{ mA cm}^{-2}$ . A survey of the current literature on OLEDs reveals that although the luminance and current density of our devices are comparable to those reported in the literature, the luminescence efficiency is still low which is possibly due to the low hole injection in the AG I layer [18, 19]. It is believed that with further studies, the electroluminescence efficiency of OLEDs formed by mist deposition can be significantly improved.

#### 4. Summary

An attempt to deposit organic semiconductor materials by mist deposition for OLED applications was made in this study. The results obtained indicate that mist deposition is capable of forming very thin, mechanically coherent films of organic semiconductors based on which OLEDs are formed. Film formation and morphology are dependent on the substrate, and



**Figure 8.** Luminance efficiency versus current density of a mist-deposited OLED.

surface preparation prior to deposition may also be needed to further improve film properties. Working OLEDs fabricated by mist deposition were also demonstrated in this study for the first time. Mist deposition shows very good promise in the deposition of thin films for organic photonics. Further studies to optimize the deposition process and hence improve the performance of the LED devices are necessary.

#### Acknowledgments

This study was supported by a SBIR program (contract no. DE-FG02-04ER83894) from The Department of Energy. Penn State authors would like to thank Agiltron, Inc. for support of this project. The deposition tool used in this study was provided by Primaxx, Inc.

#### References

- [1] Brown J, Kwong R, Tung Y J, Adamovich V, Weaver M and Hack M 2004 Recent progress in high-efficiency phosphorescent OLED technology *J. Soc. Inf. Disp.* **12** 329–32
- [2] Hatwar T K, Brown C T, Cosimbescu L, Ricks M L, Spindler J P, Begley W and Vargas J R 2004 Development in OLED formulations with improved efficiency and stability *Proc. SPIE* **5519** 1–11
- [3] Kowalsky W, Gorn P, Meyer J, Kroger M, Johannes H H and Riedl T 2007 See-through OLED displays *Light-Emitting Diodes: Research, Manufacturing, and Applications XI, 2007 Proc. SPIE* **6486** 64860F
- [4] Nomoto K, Hirai N, Yoneya N, Kawashima N, Noda M, Wada M and Kasahara J A 2008 A high-performance short-channel bottom-contact OTFT and its application to AM-TN-LCD *IEEE Trans. Electron Devices* **52** 1519–26
- [5] Mizukami M *et al* 2006 Flexible AM OLED panel driven by bottom-contact OTFTs *IEEE Electron Devices Lett.* **27** 249–51
- [6] Duggal A R, Heller C M, Shiang J J, Liu J and Lewis L N 2007 Solution-processed organic light-emitting diodes for lighting *J. Disp. Technol.* **3** 184–92
- [7] Minakata T and Natsume Y Highly crystalline thin films of pentacene formed by simple solution process and their FET performances *Proc. Int. Symp. Super-Functionality Organic Devices, IPAP Conf. Series* **6** pp 140–5

- [8] Waldauf C, Schilinsky P, Perisutti M, Hauch J and Brabec C J 2003 Solution-processed organic n-type thin-film transistors *Adv. Mater.* **15** 2084–8
- [9] Park S K, Jackson T N, Anthony J E and Mourey D A 2007 High mobility solution processed 6, 13-bis (triisopropyl-silylethynyl) pentacene organic thin film transistors *Appl. Phys. Lett.* **91** 063514
- [10] Mumbauer P, Brubaker M, Roman P, Grant R, Chang K, Mahoney W, Lee D O, Shanmugasundaram K and Ruzyllo J 2004 Mist deposition in semiconductor device manufacturing *Semicond. Int.* **27** 75–80
- [11] Zhu T, Shanmugasundaram K, Price S C, Ruzyllo J, Zhang F, Xu J, Mohny S E, Zhang Q and Wang A Y 2008 Mist fabrication of light emitting diodes with colloidal nanocrystal quantum dots *Appl. Phys. Lett.* **92** 023111
- [12] Lee D O, Roman P, Wu C T, Mumbauer P, Brubaker M, Grant R and Ruzyllo J 2002 Mist deposited high-k dielectrics for next generation MOS gates *Solid-State Electron.* **46** 1671
- [13] Shanmugasundaram K, Chang K and Ruzyllo J 2005 Effect of silicon surface condition on film formation using mist deposition *Cleaning Technology in Semiconductor Device Manufacturing IX* 1 105–10 ECS Trans.
- [14] Heyns M, Mertens M P, Ruzyllo J and Lee M Y M 1999 Advanced wet and dry cleaning coming together for next generation *Solid State Technol.* **42** 37
- [15] Shanmugasundaram K, Chang K, Shallenberger J, Danel A, Tardif F, Meillerot M and Ruzyllo J 2004 Reversing of silicon surface aging by lamp cleaning *Electrochem Soc. Proc. 8th Int. Symp. on Cleaning Technology in Semiconductor Device Manufacturing* ed J Ruzyllo, T Hattori, R Opila and R Novak vol PV 2003-26, pp 108–15
- [16] Kim K Y and Marshall W R Jr 1971 Drop-size distributions from pneumatic atomizers *AIChE J.* **17** 575
- [17] Chang K, Shanmugasundaram K, Shallenberger J and Ruzyllo J 2007 Studies of Hf (Si, O) dielectrics for metal-oxide-semiconductor applications *Thin Solid Films* **515** 3802–5
- [18] Huang J, Hou W J, Li J H, Li G and Yang Y 2006 Improving the power efficiency of white light-emitting-diode by doping electron transport material *Appl. Phys. Lett.* **89** 133509
- [19] Huang J, Li G, Wu E, Xu Q and Yang Y 2006 Achieving high efficiency white polymer light emitting devices *Adv. Mater.* **18** 114