

Surface energy patterning for continuous coating processes: A route to high throughput organic lighting and signage devices

Juliane Gabel, Charlotte Kjellander, Ike de Vries, Ronn Andriessen (*),
and Paul Blom (**)

(*) Holst Centre
TNO, High Tech Campus 31, 5605 KN Eindhoven, The Netherlands

(**) InnoPhysics B.V.
Fransebaan 592A, 5627 JM Eindhoven, The Netherlands

Presented at the 15th International Coating Science and Technology Symposium,
September 13-15, 2010, St. Paul, MN¹

Abstract

Organic electronics is a fast developing research field aiming at light-weight, low-cost, and large area applications. Roll-to-roll (R2R) processing on flexible substrates meets these demands. Deposition technologies such as slot die and kiss coating provide very homogeneous layers, which is required for organic light emitting diodes (OLED). Unfortunately, these two technologies are limited regarding the patterning of the deposited materials. For slot die coating, intermitted coating or the use of shims are two options. However, they limit the design possibilities to rectangular shapes and the definition of the edges is not sufficient. To overcome this problem we modify the surface energy of the substrate and make use of self-organized patterning of the deposited materials. Here we discuss the self-organization of slot die coated multilayered OLEDs considering i) the chemistry and processing of the surface energy patterns, ii) the physical processes of dewetting and flow to the desired patterned areas, and iii) the implementation of fundamental insight to optimize the layout and processability of OLED-based lighting and signage devices. Modeling and coating results as well as R2R compatible manufacturing of the patterns will be presented.

Modeling

Wetting is driven by minimizing the Gibbs free energy at all interfaces of the ink, the substrate and the surroundings. The energy minimization determines the final layer in terms of ink spreading, layer coverage, homogeneity and adhesion. By developing understanding on the interactions between substrate and ink, we manipulate the wetting of the ink during the device processing steps. The contact angle θ is a qualitative measure of the wetting of a solid surface by a liquid. Already in 1805 Young formulated the relationship between the interfacial tensions at the 3-phase contact line in the case of thermodynamic equilibrium (see Figure 1):

$$\sigma_S = \gamma_{SL} + \sigma_L \cdot \cos \theta \quad (1)$$

Equation (1) describes the molecular interactions at macroscopic scale during equilibrium, i.e. when no dynamic processes are involved. The contact angle mirrors the interactions of numerous molecules at the interfaces and is sensitive to small variations of the surface, such as interface reactions, presence of absorbed molecules of a third

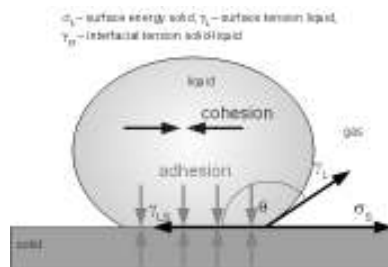


Figure 1: Interfacial interactions of a droplet on a solid surface

¹ Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

component at the interface, and microscopic heterogeneity of the surface (roughness). Some of these issues can be difficult to control or even be undesired. On the other hand, they can also be used to tailor the surface energy.

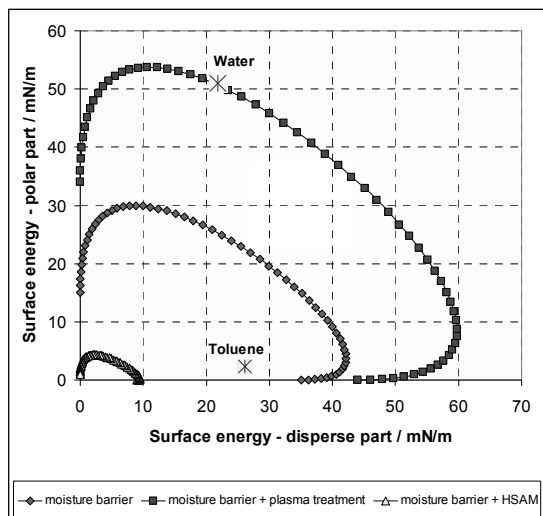


Figure 2: Wetting envelopes for $\theta = 0^\circ$

poly(ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) and light emitting polymer (LEP), required for the fabrication of OLEDs. The surface energy of the untreated substrate is much lower than the surface tension of the water-based ink. For this reason a high contact angle and poor wetting of the substrate can be expected. With a plasma treatment the surface energy can be increased to about 80 mN/m (top curve) leading to a larger wetting envelop including the coordinates of the PEDOT:PSS ink which means good wetting and spreading of the ink. The application of a hydrophobic self-assembled monolayer (HSAM) leads to a very low surface energy of about 10 mN/m (lowest curve). Neither water nor toluene will wet the HSAM surface.

The self-assembly of liquids/inks by surface energy patterning has been applied in printing technologies as e.g. off-set printing. Also the use for patterning of aqueous solutions in R2R coating processes has been demonstrated [1]. However, here we stretch the technology towards the coating of both water- and solvent-based inks in order to obtain very thin layers (dry layer thickness ≤ 100 nm). Figure 3 gives a schematic overview of the coating and patterning process. In a continuous coating process, such as slot die or kiss coating, the ink will be first applied over the full area (top). Growing perturbation in the liquid film on top of the hydrophobic area finally leads to film break-up and dewetting (middle). In the final stage the liquid film has to stabilize in the hydrophilic zone (bottom).

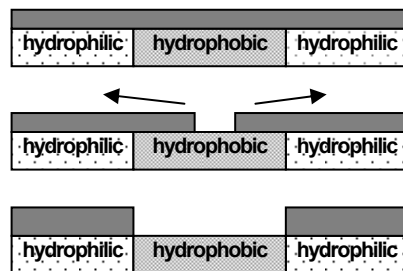


Figure 3: Schematic representation of the surface energy-induced patterning

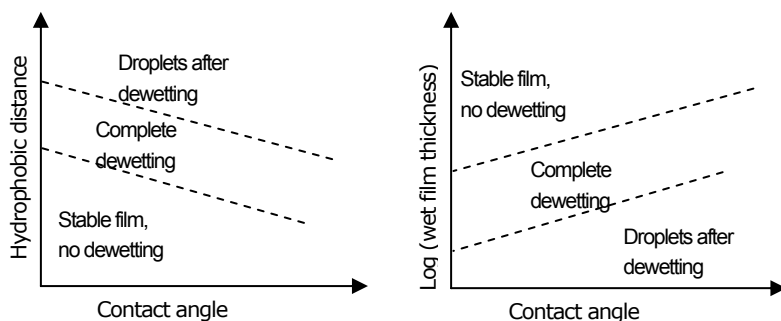


Figure 4: Dewetting influencing parameters; left - hydrophobic distance vs. contact angle, right - wet film thickness vs. contact angle

To predict how well a surface is wetted by a liquid, we compare the air-liquid interfacial energy of the ink (surface tension) with that of the surface using a model involving two energy contributions, i.e. the polar and disperse contributions to the total energy. The method yields a 2-dimensional plot, the so called wetting envelope (Figure 2). A prediction of an ink's wetting behavior is obtained by comparing the surface tension of the ink with the wetting envelope of the surface. Complete wetting is obtained for an ink with disperse and polar coordinates within the area confined by the x- and y-axis and the curve for $\theta = 0^\circ$ and partially wetting occurs for inks with polar and disperse coordinates lying outside of the envelop. For large contact angles ($\theta \geq 90^\circ$) spontaneous dewetting will occur. Figure 2 shows wetting envelopes for a PEN foils with a moisture barrier as applied in the production of flexible OLEDs. The untreated substrate (middle curve) has a surface energy of about 50 mN/m. The graph also contains the coordinates of water and toluene. These fluids respectively represent the solvent media for inks containing

The dewetting process is constrained by several parameters. Experiments showed that depending on the interplay between film thickness, width of the hydrophobic area, and contact angle, the film may i) retract completely, ii) retract incompletely, leaving droplets in the hydrophobic zone, or iii) be stable and not retract at all [2]. Figure 4 gives an overview of the relations between these parameters. As shown by the graphs, there is only a limited range for perfect dewetting. For low contact

angles and thick wet layers dewetting might not occur, whereas large contact angles and thin wet films favor complete dewetting. In the case of narrow hydrophobic areas, the liquid film might bridge the hydrophobic area even for high contact angles, whereas for an increasing hydrophobic distance the chance of droplet formation increases.

In R2R coating processes the wet film thickness is a more or less fixed parameter, defined by the application. Functional organic layers for OLED devices have a dry layer thickness in the range of 50 to 200 nm. Solute concentration constraints defined by polymer solubility and/or ink viscosity result in wet film thicknesses typically in the range of 10 to 20 μm . It appears that the operational window for the hydrophobic zone dimensions becomes very narrow. For hydrophobic paths of < 1 mm bridging will occur, whereas for larger distances droplet formation will be observed. Regarding the high surface tension (> 65 mN/m), for water based PEDOT:PSS ink complete dewetting can be expected for several mm hydrophobic distance while for the low surface tension (< 30 mN/m) LEP ink with a low surface tension droplets will be formed already at short distances.

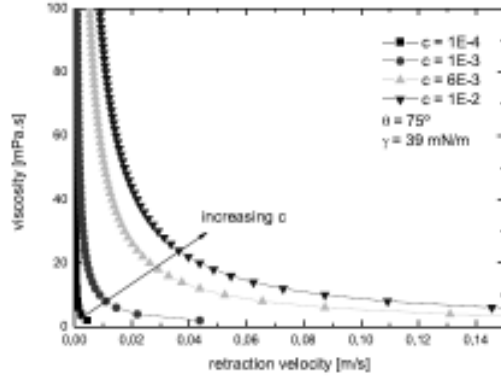


Figure 5: Retraction velocity vs. viscosity

Equation (2) expresses the relation between viscosity (η), surface tension of the ink (γ), and contact angle (θ). c is a system-dependent numerical constant. The energy difference, here expressed by θ , is the driving force for dewetting. In general, the retraction velocity decreases with increasing viscosity; the fastest retraction is achieved for the lowest viscosity. However, the involved coating process requires a certain viscosity range [5].

During drying the concentration of the solution increases. Polymer-based inks show an exponential increase of viscosity with increasing concentration (see Figure 6). As already mentioned, liquid retraction slows down with increasing viscosity, and therefore it is preferable to gain complete dewetting before the coated web reaches the drying unit, where fast evaporation of the solvent occurs. For this reason, the maximum retraction time (t_{max}) is equivalent to the quotient of the distance between coating unit and dryer (D) and the line speed (v_{R2R}):

$$t_{\text{max}} = \frac{D}{v_{R2R}} \quad (3)$$

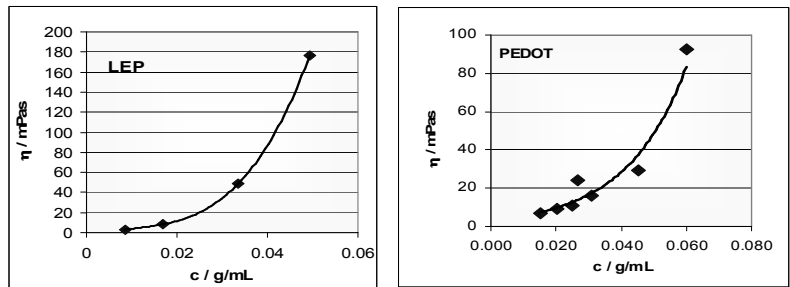


Figure 6: Viscosity vs. concentration, left - LEP ink, right - PEDOT ink

Experiments and Results

Surface energy patterns can be obtained in two ways: i) selective deposition of hydrophobic material or ii) homogeneous deposition of a hydrophobic material followed by selective removal. For OLED-based applications, the use of SAMs is preferred owing to their low layer thickness. However, patterned deposition of these materials might not be easily translated into a R2R process. On the other hand, it was already pointed out that the moisture barrier layer needs plasma pre-treatment to achieve optimal coating conditions. So, by combining the homogeneous deposition of a HSAM followed by selective removal during a plasma treatment, hydrophobic/hydrophilic patterns for optimal coating and dewetting can be obtained.

Fluorinated trichlorosilanes were chosen as precursors for the HSAMs. These molecules readily bind to the inorganic top-layer of the moisture barrier, even at room temperature, requiring no surface pretreatment. The HSAM can be deposited using a R2R atmospheric pressure chemical vapor deposition system (AP-CVD) as shown in Figure 7. The deposition has been demonstrated successfully with speeds up to 5 m/min. Dynamic contact angle measurements indicate that the deposited layers are not perfect in terms of molecular packing. However, preliminary experiments showed that even in the presence of small faults in the hydrophobic layer, decent dewetting properties can still be obtained. The hydrophobic layer prepared by AP-CVD had a total surface energy of < 10 mN/m, comparable to stationary, sheet-processed samples (see also Figure 2).

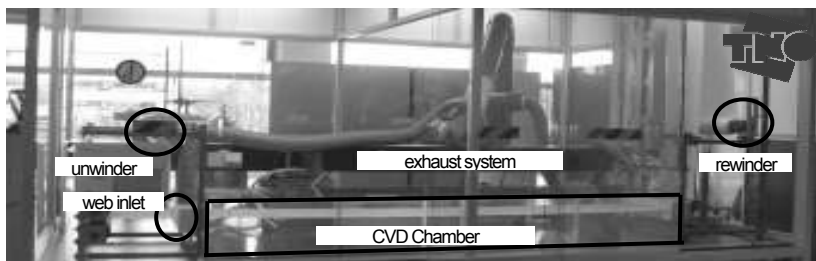


Figure 7: R2R atmospheric pressure CVD system for HSAM deposition

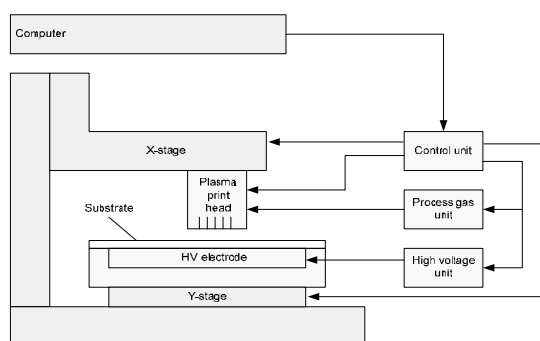


Figure 8: Schematic representation of the plasma printer [6]

Plasma printing has been successfully demonstrated on a sheet-to-sheet level and can be up-scaled to R2R.

Figure 9 shows a sample containing R2R slot die coated PEDOT:PSS and LEP layers. The HSAM was patterned using the masking method. The sample was coated with a speed of 5 m/min and the distance between coating unit and oven was about 0.5 m. Theoretically calculated, using equation (1) and (2) the inks will spontaneously dewet the HSAM surface and the time of dewetting is faster than the maximum calculated retraction time. As expected is the PEDOT:PSS ink retracting spotlessly from the hydrophobic area whereas the low surface tension LEP ink leaves droplets behind (seen as the white spots in the dark areas in Figure 9). To gain deeper insight in the dewetting processes we are currently investigating the surface interactions and drying behaviors experimentally and by numerical modeling methods.



Figure 9: Slot die coated PEDOT:PSS and LEP layers, patterned by surface energy

Acknowledgements

The authors would like to thank Gerwin Kirchner, Arjan Langen, Timme Lucassen, Jasper Michels, Twan van Schijndel, Mirjam Theelen, and many others for experimental help and fruitful discussions.

The Holst Centre is an open innovation research centre founded by TNO and IMEC that is developing R2R production techniques for foil-based organic electronics and wireless autonomous transducer solutions, in cooperation with industry and universities.[7] This particular research has been funded by the Dutch Ministry of Economic Affairs, Philips Research, Merck and Agfa.

References

- [1] Bower et al AIChe J. 53 (2007) 1644-1657
- [2] For information about modeling of this behavior see the contribution of B. Brasjen et al.: "Coating and stability of thin liquid films on chemically patterned surfaces"
- [3] Bouchard-Wyart, de Gennes, Adv. Col. Interface Sci. 39 (1992)
- [4] Bouchard-Wyart, de Gennes WO2005/014184A1
- [5] For information about viscosity of inks see the contribution of J. Michels "Viscosity control of Light-Emitting Polymer Inks for Large Area OLED processing"
- [6] For more information see: www.innophysics.nl
- [7] For more information see: www.holstcentre.com