Printin process development for fabrication of organic electronic devices is described, with focus on semiconductor layers for organic light-emitting diodes and photovoltaic cells. This development is considerably more complex than for a graphical printing process. Key aspects are an adequate dosing and transfer of highly volatile inks, the reliable coalescence of the droplets deposited on the substrate to a closed liquid film, and the successful relaxation and leveling of the liquid–air interface in the solvent evaporation phase in the presence of Marangoni stresses and pattern formation instabilities. The conditions for successful implementation of a gravure or inkjet process, using steadily developing, new generations of polymer as well as small molecule semiconductors are, to a large extent, but not exclusively, originating from the molecular features of organic semiconductors and their printable solutions. In addition, recent developments in surface technology, and in the physics of thin-film dynamics and spontaneous pattern formation contribute to a proper understanding of liquid layer dynamics in printed electronics. The role of ink formulation, Marangoni stresses related to concentration and temperature gradients, the effect of the disjoining pressure, and solvent evaporation are discussed.

1. Introduction

The appeal of organic electronics, lasting for almost two decades now, comes from the option of using cost-efficient and flexible printing technologies for the production of a new type of electronics, heralding a fascinating new era of flexible, cheap, resource-saving and ubiquitous communication, lighting, and energy technology. Digital circuits of organic thin-film-transistors (OTFT), photovoltaic cells (OPV), or light-emitting diodes (OLED) could be manufactured at a fraction of fabrication invest and material expenses of conventional silicon chip manufacturing facilities.[1,2] Apart from the continuous development of many different novel and increasingly powerful organic semiconductors, printing contributes efficient technologies for solution-based processing of material layers of optical quality with thicknesses originally reserved for vacuum deposition technologies, i.e., 10–30 nm. These novel technologies open new applications in different industries: surface technology, packaging, biomedical technology, and, of course, electronics.[3]

However, the technology development from graphical to functional printing had to face, in some places, major obstacles which are deeply anchored in the principal physics and chemistry of, in particular, organic semiconductors and their solvent-based solutions.[4,5] So, if we refer to gravure, inkjet, flexographic printing in the sequel, this does not imply that the printing process, the design of machines and printing forms, and ink formulations are the same as, or even suited for graphical reproduction. The task is complex, and it is adequate to distinguish three fields within printed electronics, where the requirements imposed on printing technologies can be considered as being more or less independent: OLED/OPV, OTFT, and high-resolution printing of conductive patterns for, e.g., sensor applications and source and drain of OTFTs. We shall restrict here to three typical examples. A more general overview is given in the book of Nisato et al.[2]

From the printer’s point of view, the principal challenge of OLED and OPV devices is the creation of thin, defect-free, and homogenous layers of a semiconductor under the conditions imposed by diluted and highly volatile solutions of the respective semiconductor compound. Typical layer thicknesses are of order of 10–100 nm for OLEDs[6,7] and 100–400 nm for photovoltaic cells.[8] Lateral sizes of such devices are in the range of centimeters (on the lab scale) to meters (in future applications). Printing technologies that could meet, and which offer the option of satisfactory product throughput, are gravure and inkjet printing.[8] Both technologies can deal with fluids of lowest viscosity and limit the contamination of the partly very sensitive semiconductors with air, humidity, or particles to an inevitable minimum, compared to other printing technologies.[3] Moreover, ink formulations adequate for inkjet are frequently also suited for gravure, and vice versa. On the lab scale, it may be useful to try both, and also to compare the printing result with samples from spin coating. Neither inkjet nor gravure printing...
is able to deposit closed liquid layers, but create arrays of sepa-
rated droplets of printing liquid on the substrate. These dro-
plets have diameters of 10–50 µm, and capillary forces must
be employed to create a closed film, and to attach them to the
substrate. One needs to implement concepts to control drop
coalessence, layer formation and leveling, and solvent evapa-
tion. This, in turn, implies that spontaneous pattern formation
and Marangoni effects could become important. In this article,
we shall focus on this aspect of electronic printing, as it seems
that the printing research activities of the Forum Organic Elec-
tronics within the Innovation Lab have contributed the most
fruitful insight and exciting progress here.[6,7,9]

The second field of printing research deals with the semicon-
ductor layer which has to be placed on top of the source–drain
electrode structure of an organic thin film transistor (OTFT).
Again, the task here is to place a thin layer of an organic semi-
conductor on a prestructured surface. Printing such electrodes
is at the resolution limit (≈10 µm) for any printing and liquid
processing technology.[10] This turns out to be another challenge
of the OTFT topic. Gravure printing technology offers adequate
solutions using direct[11] or indirect[12] pattern replication. How-
ever, process and ink concepts are highly specific. OTFT printing
exemplifies the need that printed electronics calls for a portfolio
of unique, highly adapted methods for each of the numerous
materials that have to be combined to an overall process for an
electrically useful device.[3] Printing ink formulations for OTFT
devices and their properties, e.g., for a bottom-contact transistor
design, resemble the OLED inks in many respects. For the
printer, the issue is even less ambitious, and the requirements
on lateral layer homogeneity and defect formation are much less
rigorous. Coffee stain formation and Marangoni effects in the
drying semiconductor spot, as in the OLED printing problem,
can be kept under control by the choice of the printing pattern,
specifically by deliberate placement and pinning of the contact
line of the volatile surface of the liquid drop or film with the sub-
strate surface.[13] There is hardly any place on the OTFT where
printing resolutions below few 100 µm, or layer homogeneities
over distances beyond few nm are required.

The third area of printed applications relevant for electronics
refers to conductive structures as, e.g., current-conducting bars,
nontransparent electrode structures or contact pads for, say, elec-
troluminescent panels, printed batteries, solar cell back, and,
sometimes, transparent front electrodes.[34] Typically, these struc-
tures are printed using concentrated preparations of nano- or
micrometer-sized metal and metal oxide particles, with a rheology
close to gelation. This type of printing is readily established in
electronics manufacturing, and the very domain of flexography
and screen printing. This printing technology is capable to handle
dispersions and slurries of particles, and to operate with liquids of
large and structural viscosity. Solidification and liquid film insta-
bilities, and Marangoni effects are inoperative here. Such issues
could be easily removed with printing ink additives, thickeners,
and dispersion agents. This option is never at the printer’s dis-
posal when processing organic semiconductor solutions.

The reader may notice that prominent technologies from
graphical arts are almost missing here: offset lithography and
flexography. This is partly due to the complexity of the physics
and chemistry behind the materials used there, the role of
hydrophilic and hydrophobic interfaces. We should like to
emphasize that there are considerable examples for a successful
implementation of offset lithography[15,16] and flexography[7,14]
in printed electronics. In this paper, we shall skip these topics,
as many findings of principal importance can also be demon-
strated with conceptually minimalist printing techniques such as
gravure and, in essence, inkjet.

In the subsequent section, we shall give a principal description
of the process and the critical parameters of the fluid dosing and
transfer by a gravure printing unit. We shall discuss the role of
the leveling process of the deposited liquid film and the conditions
for the formation of a homogenous layer. This is done in view of the
specific ink formulations used in OLED, OPV, and OTFT printing
processes, i.e., a dilute solution of a polymer or small molecule
semiconductor in a volatile organic solvent. We shall further argue
why evaporation and Marangoni stresses in the liquid layer may
become dominant for the whole deposition process. We close with
a discussion of the parameter ranges where one may expect that
the formation of a homogenous layer with a thickness in the range
of few 10 nm can be expected after transition to the solid state and
complete evaporation of the solvent. This part applies not only to
the gravure process, but also to inkjet or flexographic printing as
far as similar ink formulations are used.

2. Ink Dosing for Organic Semiconductor Layers

2.1. Transfer Volume, Layer Thickness, and Solute Concentration

Semiconductor layers of OLED and, in part, of OPV devices
require layer thicknesses of 10–100 nm. We refer to this as “ultra-
thin,” meaning that they cannot be considered to be large com-
pared to the range of Van der Waals interaction,[17] electrostatic
screening, or the diffusion range of molecules within liquid film
time. Moreover, capillary forces of fluid menisci on this scale are
by far dominating viscous forces and gravity by orders of magni-
tude. Precise dosing and transfer of correspondingly small quan-
tities of ink to a specific position on the printing substrate by
any printing technology like inkjet or gravure printing is not pos-
sible. As an example, the extrusion of a 100 nm toluene droplet
from the nozzle of an inkjet print head or from a gravure cell
requires an ink pressure of 3 bar to overcome capillarity. Typ-
ical sizes of ink drops are 10–30 µm. This is dictated by hydro-
dynamics, and feasibility can be quantified in terms of capillary,
Weber, and Ohnesorge (or Laplace) numbers as discussed, e.g.,
in a recent review of Kumar.[38] The printer thus operates with
highly diluted ink formulations, with a concentration of 1–2 wt% of
material. The printed layer is assembled from picoliter drop-
lets. The final solid film thickness, being smaller by orders of
magnitude, is the achievement of solvent evaporation, and of set-
ing deliberate conditions for liquid film leveling. Consequently,
the design of gravure printing cylinder serves the optimization of
droplet coalescence on the substrate or in the printing nip,
setting conditions for efficient liquid film leveling.

2.1.1. Defining a Gravure Cylinder

The key component of a gravure printing unit is the gravure
cylinder, which is responsible for both precise dosing and
deposition of the printing ink. This is achieved by the gravure cells. In a continuous rotational motion with a circumferential velocity $v_p = 0.5$–$5 \text{ m s}^{-1}$, the cells are filled with printing ink. Abundant ink is then removed from the cylinder surface by a doctor blade, and the inked cylinder is rolled over the substrate at constant velocity $v_p$. A considerable normal force of up to $4 \text{kN per meter of cylinder width}$ is exerted such that the walls between the gravure cells are in mechanical contact to the substrate surface. The capillary forces inside the residual, microscopic gap between the surfaces drag the ink out of the cells.

Conventionally, gravure cylinders are created by electromechanical engraving on a lathe. In this process, an orthorhombic raster of cells is engraved into the copper-plated surface of a steel cylinder. Each cell roughly has the shape of an inverted pyramid. One of the diagonals of this pyramid is oriented in direction of cylinder circumference, i.e., in printing direction. The raster is characterized by its raster angle and the raster width. In crystallography, these parameters would be referred to as lattice constant and angle of the orthorhombic unit cell. Gravure rasters of widths in the range between 20 and 150 µm, and raster angles of $15^\circ$ to $75^\circ$ are useful and technologically possible for engraving lathes of commercial suppliers of printing equipment. An example is shown in Figure 1.

In the engraving process, the volume of the cells is determined by the penetration depth of the gravure stylus. Cell volume may be individually defined for each cell, but all cells are congruential, i.e., they have the same ratio of depth and width. The depth $d$ is typically in the range between 0 and 40 µm. With these parameters, specifically raster width and cell volume, the printer is able to determine droplet volume and distribution on the substrate. When printing semiconductor layers for electronics, cell volume is usually kept constant over the desired printing area of the gravure cylinders. Variations in cell volume at the border of the printed area could be considered in order to improve the edge sharpness, to flatten coffee-stain walls at the rims of the printed area on the substrate, or to compensate capillarity-driven dewetting at sharp edges of the printed pattern.

Gravure cylinder radii $R_c$ range from 3 cm on the lab scale to 50 cm on the production scale. It has often been believed that this parameter is of minor principal importance in the printing process, specifically if the lateral size of the printed pattern is small compared to $R_c$. A recent study, however, has revealed a surprising effect of the cylinder radius on the hydrodynamics of cell emptying flows in the printing nip. The key observation is that the characteristic hydrodynamic length scale defining the fluid flow is $H = (R_c d)^{1/2}$, and significantly depends on the cylinder radius. This length scale is of the order of 1 mm, typically. By the dynamics of ink splitting in the printing nip, it appears as the characteristic scale of viscous finger formation, or ribbing instability. The perturbations in the freshly deposited liquid film inherit this length scale. Consequently, the efficiency of capillary leveling of the evaporating liquid film is changed. The residual inhomogeneity of the dried layer in a printed OLED may thus change its morphology with the transition from small lab scale to industrial-size cylinders. In the processed OLED device, homogeneity of light emission and visual appearance could develop new patterns on the millimeter scale in the course of process upscaling as a consequence of shifting the hydrodynamic scales of the solution-based process.

2.2. Ink Dosing and Transfer

2.2.1. Substrate Wetting and Ink Splitting

It is apparent that the gravure volume of the printing cylinder should be adequately metered for the formation of a closed liquid film on the substrate. The continuous wetting of the substrate with ink is not a function of the equilibrium contact angle between ink and substrate. For a short instant, shear and capillary forces in the nip exceed solid–liquid adhesion forces by orders of magnitude. Provided that the gravure volume exceeds a certain minimum value, liquid ink bridges are created across the walls between the cells in the printing nip. A continuous fluid meniscus is thus stretched over the complete width of the printing area. Microscopic air intrusions between printing cylinder and substrate are replenished at that moment by the intense capillary fluid pressure and by the shear force in the nip. A gravure press could even enforce wetting of superhydrophobic surfaces, because, as Gao and McCarthy have pointed out, finite adhesion energy across the liquid–solid interface is available even at contact angles close to $180^\circ$. Dewetting of such metastable layers is triggered by surface perturbations, thin-film instabilities, particle contamination, pinholes, or proceeds from the rim of the printed area.

Figure 2 shows an example of a printed sample of nanoscaled silver ink on glass where drop coalescence was not successful due to insufficient dosing. The deposited silver droplets have reproduced the cell raster of the printing cylinder.

If more ink is deposited than actually needed, the excess of liquid fills the wedges between cylinder and substrate, forming a continuous meniscus across the walls between the cells. This meniscus is dragged with the cylinder motion over the substrate, leaving a closed liquid film. This excess of fluid is the origin of the viscous finger or ribbing instability. It can be identified as a more or less regular pattern of ink “ribbons” of few 100 µm in width which are oriented in printing direction. Adequate gravure parameters imply a trade-off between the two extremes, and must also consider rheology and capillarity of the ink. This is discussed below.

After lift-off of the printing cylinder from the substrate, it can readily be assumed that a closed liquid film has been left on the substrate, which is, however, far apart from thermal...
and wetting equilibrium. This film can be characterized by its average thickness $h_0$, which is of the order of 1 μm, typically. However, the height profile of the liquid–air interface normally still exhibits traces of the gravure raster, and of the viscous fingering instability.

### 2.3. Liquid Layer Relaxation and Drying

#### 2.3.1. Leveling of the Liquid Film

For the printer, the key question is whether an inhomogeneity of the liquid film, given by the height profile $h(x,y,t)$ over the substrate surface, can be leveled by capillary tension at the liquid–air interface, or whether initial perturbations of the liquid film will actively grow in amplitude. Pattern formation at the liquid–air interface always creates an excess of surface, compared to an ideal, planar film. There are two main sources of energy to drive this: the interaction between the interfaces of the film with the substrate and with the gas phase. This is known as the disjoining pressure.\(^{[17]}\) The second source is the enthalpy of isothermal or adiabatic solvent evaporation into a nonsaturated gas phase: the chemical potential of a solvent molecule is larger in the liquid than in the vapor phase.\(^{[21]}\)

In addition to this, specific materials may cause instabilities in the liquid phase by transitions in their specific molecular conformation. An example for this is poly-(3-hexylthiophene) (P3HT), a polymer semiconductor frequently used for solar cells and for thin film transistors. It is soluble in organic solvents like toluene, xylene, or dioxane.\(^{[8,22]}\) Depending on the solvent, P3HT may either form an isotropic polymer solution or a dispersion of molecular, rod-like agglomerates, with a pronounced tendency to gelation.\(^{[23]}\) For the reason of optimal charge carrier mobility of the semiconductor in the electric device, the latter case is highly preferred. Crystalline order evolves in such layers after solidification, whereas the P3HT layer forming from the isotropic solution is almost amorphous, with a charge carrier mobility being inferior to the former by up to one order of magnitude. The point is, however, that the P3HT dispersion in, e.g., toluene exhibits a pronounced negative Marangoni coefficient, whereas this coefficient is close to zero for the isotropic solution, see Table 1. As will be argued, the printer then faces severe pattern formation issues in the relaxation phase, caused by a complex interaction between evaporation, solidification, and Marangoni forces.

At first, we shall give a brief overview on the general relevance of the different liquid-film forces.

#### 2.3.2. Effect of Disjoining Pressure

Disjoining pressure of liquid films results from Van der Waals attraction of its surfaces and amounts to the intrinsic pressure of the liquid phase by $p_d = -Ah^{-3}/6\pi$, where $A$ is the Hamaker constant of the solvent and $h$ is the film thickness.\(^{[24-26]}\) Liquid films of low thicknesses therefore exhibit an excess of internal hydrostatic pressure, compared to thicker films. Pressure may even oscillate as a function of film thickness, giving rise to numerous wetting phenomena at the three-phase contact line. An example is the formation of a characteristic wall, or a sequence of concentric walls which surround a pinhole, see Figure 3. Such phenomena have been studied by Reiter\(^{[27]}\) and Seemann et al.\(^{[28]}\) for thin polymer films. Their findings

![Figure 2. White-light interferometric image of a raster of gravure-printed silver dots on glass. Drop coalescence was achieved for the drops deposited at the border, but not in the bulk region. Raster width is 250 μm, and dot height is 1.5 μm, approximately.](image)

| Solute                  | Solvent, (type of liquid phase) | Solvent surface tension $\sigma$ [mN m\(^{-1}\)] | Marangoni coefficient $\sigma_0$ [mN m\(^{-1}\) (wt%\(^{-1}\))] |
|-------------------------|--------------------------------|-------------------------------------------------|-----------------------------------------------------------------|
| P3HT                    | Anisole, (a)                   | 34.7                                            | -2.0 +/- 0.3                                                     |
|                         | Toluene, (b)                   | 28.6                                            | -1.66 +/- 0.56                                                  |
|                         | Toluene, (a)                   | 28.6                                            | -0.26 +/- 0.06                                                  |
|                         | o-xylene, (a)                  | 29.6                                            | +0.18 +/- 0.10                                                  |
|                         | Toluene                        | 28.6                                            | +0.97 +/- 0.11                                                  |
| PIF8-TAA (c)            | THF                            | 26.4                                            | -1.0 +/- 0.08                                                   |
| NDI (d)                 | Toluene                        | 28.6                                            | +0.035 +/- 0.08                                                 |
| Lumogen F Red 305 (e)   | Toluene                        | 28.6                                            | +1.00 +/- 0.08                                                  |
| Polystyrene             | Toluene                        | 28.6                                            | +0.50 +/- 0.46                                                  |
| Superyellow(f)          | Toluene (80%) + benzothiazole (20%) | 30.0                                      | +4.5 +/- 0.7                                                   |
Figure 3. Coherent light interferometric profile of a Superyellow emitter film of ~50 nm in thickness, with a pin hole and its protruding wall at the rim.

remarkably resemble occasional pinhole defects in OLED layers. Such defects may induce the complete break-through of the film, and a dewetting of the substrate from the printed liquid film. The phenomenon indicates that disjoining pressure cannot generally be neglected, in particular in OLED printing. Although pinhole nucleation can be prevented by careful pretreatment of the substrates, the phenomenon raises the question whether spinodal dewetting could be driven in thin liquid films by disjoining pressure. Calculations of Bornemann et al. have indicated, however, that pattern growth time is typically larger by orders of magnitude compared to drying time. Thus, with respect to the leveling problem of printed but closed liquid films, the mechanism is probably not the dominant one.

2.3.3. Thermal versus Concentration-Related Marangoni Drag

Temperature gradients related to the latent heat of evaporating solvent could induce a thermal Marangoni drag in the liquid film. The surface tension of many liquids typically decreases by 2–3% per degree centigrade, and pattern formation phenomena driven by temperature gradients have been extensively studied by numerous authors. It is characteristic that the activity of this transport mechanism strongly increases with the thickness of the liquid film. In view of the extremely thin layers considered here, and the substantial heat capacity and comparatively large thickness of a printing substrate made of glass or polymer foil, we consider thermal Marangoni drag as small compared to the concentration-related one, which becomes dominating for thin layers. The temperature in the liquid film caused by evaporation heat can be estimated not to exceed 1° or 2°. However, depending on one film thickness one could imagine specific exceptions.

For these reasons, we shall focus our discussion on effects related to isothermal evaporation and concentration-related Marangoni drag. Examples for Marangoni coefficients of various polymer and small-molecule materials in various solvents are presented in Table 1.

Pattern formation, i.e., the spontaneous growth of an initial local perturbation of the liquid film, proceeds exponentially in time and may thus end up with a break-through of the liquid film. This, in turn, could initiate a possible progressive deterioration of the liquid film. Marangoni-related pattern formation could be avoided, at least in part, using mixtures of different solvents. The strategy is to take a combination of a solvent with high vapor pressure, and low surface tension, and another one of smaller vapor pressure and larger surface tension. The more volatile component evaporates faster. Its concentration in the liquid layer shrinks, and surface tension of the mixture rises in time. In the optimal case, this can compensate a possible negative Marangoni coefficient of the dissolved semiconductor material. This has been studied by Hernandez-Sosa et al., using toluene–benzothiazole mixtures for polymer OLED printing.

3. Liquid Film Leveling Model

3.1. Leveling Forces

Leveling of liquid films is the effect of at least four different transport phenomena which are simultaneously active: capillary leveling of the liquid film surface, lateral solute diffusion, solvent evaporation into the gas phase, and Marangoni drags related to possible gradients of solute concentrations. In our liquid film leveling model, the decrease of solvent vapor pressure over the liquid according to Raoult’s law is taken into account as well. Thermal Marangoni drag and disjoining pressure are omitted. We consider this to be second order in average practice. Specifically, it is assumed that solvent evaporation from the liquid film is not supported by active heating.

3.1.1. Height Profile and Solute Concentration

A two-component liquid film can be characterized by its height profile \( h(x,y,t) \) in the \( xy \)-substrate plane and by local solute concentration, given by the molar fraction \( \phi(x,y,t) \) of the solute. Lateral solute diffusion contributes to liquid film relaxation by reducing possible concentration gradients. With respect to the transversal, or \( z \), direction, we assume that the chemical potential \( \mu(\phi) \) of the solvent inside the liquid film is constant, i.e., \( \frac{d\mu(\phi)}{d\phi} = 0 \), and matches continuously with the chemical potential of solvent molecules in the adjacent gas phase (where it develops a significant gradient, driving vapor transport) and, if imbibition or swelling is significant, in the substrate surface. This is physically consistent with the assumption of a concentration-related Marangoni drag in the liquid film. By Gibbs’ rule, this implies transversal concentration gradients, i.e., an enrichment or depletion of the liquid surface with solute molecules, at constant chemical potential. Relaxation is described by the following set of two coupled equations for \( h \) and \( \phi \). We assume that no solid phase has deposited. Nonlinear terms in the gradients of \( h \) and \( \phi \) are skipped

\[
\frac{\partial h}{\partial t} = -\nabla \left[ \frac{h^3 \sigma}{3 \eta} \nabla h + \frac{h^2 \sigma_e}{2 \eta} \nabla \phi \right] + u_e (\phi - \phi^{(eq)}) \tag{1}
\]

\[
\frac{\partial \phi}{\partial t} = D_e \Delta \phi + u_e \frac{\phi}{h} (\phi - \phi^{(eq)}) \tag{2}
\]
Equations (1) and (2) describe the time-development of the height profile \( h(x,y,t) \) and the solute concentration \( \phi(x,y,t) \) (in units of molar fraction) of the liquid film. The first term of Equation (1) in square brackets describes the leveling of the liquid film surface by capillary forces. Here, \( \sigma \) and \( \eta \) denote the surface tension and the viscosity of the liquid, respectively. The second term in the square bracket describes Marangoni drag of the liquid film, driven by the gradient of solute concentration \( \phi \). The coefficient \( \sigma_\phi = \partial \sigma / \partial \phi \) specifies the change of surface tension with solute concentration \( \phi \) at constant temperature and will be discussed in detail below. The third term in Equation (1) describes the solvent evaporation. The coefficient \( u_e \) denotes the evaporation rate of the solvent over the liquid film under the given atmospheric conditions. Some examples are given in Table 1.

### 3.1.2. Solvent Evaporation and Condensation

Solvent evaporation from a liquid film is limited by the diffusion of solvent vapor in the gas phase. As a matter of fact, evaporation constitutes a complex phenomenon of diffusive and convective gas transport. On an industrial-scale printing machine, specific drying units are provided. In the lab, sufficiently reproducible drying conditions are usually implemented by placing the lab scale printability tester in the flue. Also in the present model, drying is specified by two heuristic parameters, the evaporation velocity \( u_e \) and the equivalent concentration \( \phi^{(eq)} \). The evaporation velocity can be determined for the printing setup from the observation of the evaporation \( T_e \) time of a liquid film of pure solvent with known initial thickness \( h_L \) under fresh air by \( u_e = h_L/T_e \). With \( \phi^{(eq)} \), we characterize the solvent vapor pressure of the drying atmosphere which is actually used in the printing experiment, and which takes up the solvent vapor from the liquid film. \( \phi^{(eq)} \) denotes the concentration of a (fictitious) liquid solution of the same solvent and solute that is in equilibrium with the drying atmosphere, which may be partly saturated. Solvent evaporation from the liquid film requires that \( \phi < \phi^{(eq)} \). In case of \( \phi > \phi^{(eq)} \), solvent vapor from the atmosphere condensates in the liquid film. The first term on the right-hand side of Equation (2) describes the lateral diffusion of the solute in the liquid film, and \( D_s \) is the corresponding diffusion constant of the solute in the liquid phase. The second term in Equation (2) denotes the effect of concentration increase in the liquid film by ongoing solvent evaporation. The film thickness \( h \) appears in the denominator. This accounts for the feature that surface-to-volume ratio of the fluid film increases with decreasing film thickness. This is also consistent with Raoult’s law. We emphasize that both equations are only applicable up to the point where the segregation or deposition of a solid phase begins.

### 3.2. Liquid Film Stability Analysis

#### 3.2.1. Wavelength and Amplitude of Perturbations

Equations (1) and (2) have an obvious solution which describes a liquid film of laterally constant thickness, with thickness \( h_0(t) \) continuously decreasing to \( h_\infty \), and \( \phi_0(t) \) approaching unity, the solid state limit of the layer. This solution describes the desired situation in the printing and evaporation process, a homogeneous solid layer of the OLED semiconductor. Small perturbations of this homogenous solution can be written as

\[
h(x,y,t) = h_0(t) + h_e e^{i(k_x x + k_y y + \omega t)}
\]

\[
\phi(x,y,t) = \phi_0(t) + \phi_e e^{i(k_x x + k_y y + \omega t)}
\]

where \( h_e \) and \( \phi_e \) are the amplitudes of perturbations in the substrate plane with wave vector \( \vec{k} = (k_x, k_y) \), and \( \Lambda_{1,k} \) and \( \Lambda_{2,k} \) are the respective relaxation rates.

#### 3.2.2. Basic Solutions

If both rates are positive and \( \Lambda_{1,k} \) large compared to the evaporation rate, and if thickness and concentration modes decouple sufficiently, one asymptotically obtains

\[
\Lambda_{1,k} = \frac{\sigma k h_e^2}{3\eta} \quad \text{(5)}
\]

\[
\Lambda_{2,k} = D_s k^2 \quad \text{(6)}
\]

Equations (5) and (6) are the capillary leveling equation for the height profile of a one-component liquid film and for the diffusion-driven decay of concentration gradients. For a gravure or inkjet printed layer both equations claim that a liquid layer created from deposited droplets will level, and that possible concentration gradients will disappear exponentially for any wave vector \( \vec{k} \). Leveling may be slow for small \( \vec{k} \), i.e., at large length scales, or wavelengths \( \lambda \). Any such perturbation of the layer may result in a thickness modulation of the solid film. In particular, when a layer of the OLED stack is printed, this can easily be recognized by the optical interference of light in the liquid film at the interface to the transparent anode. Conventionally, the transparent base electrode made of indium tin oxide (ITO) is of great advantage here. By its large refractive index, compared to the organic material, it guarantees and air it provides optimal optical contrast for the Newtonian rings, which reflect the local layer topography \( h \). Such interference patterns can relatively efficiently be recorded by a digital camera, and used for in-line thickness measurements. Such measurement technologies, essentially based on the time-resolved observation of Newtonian rings at different optical wavelengths, have extensively been studied in the research collaborations at the Forum Organic Electronics, and are known as imaging color reflectometry (ICR). This can be used not only in order to determine the respective wavelength and amplitude of a progressing instability, but also to identify the time and film thickness when it is initiated.

#### 3.2.3. Effects of Solvent Evaporation and Marangoni Drag

However, the ideal situation indicated in Equations (5) and (6) hardly ever applies in practice. Already at first order in the...
perturbation amplitudes it becomes apparent that leveling is not generally possible, i.e., thickness and concentration undulations do not decouple. Inserting Equations (3) and (4) into Equations (1) and (2), skipping higher-order terms, one obtains the following dynamic matrix for relaxation and pattern formation in the liquid film

$$H = \begin{pmatrix}
-D_k^2 - \frac{2\phi_h - \phi^{(eq)}}{h_0} & \frac{2\phi_h - \phi^{(eq)}}{h_0} \\
\frac{h_0 k^2}{2\eta} & \frac{\sigma \phi h_0 k^2}{3\eta}
\end{pmatrix}$$ (7)

The dynamic matrix is a function of $h_0(t)$ and $\phi_h(t)$ and thus time-dependent by itself. The relaxation is then described by the following equation

$$\frac{d}{dt} \begin{pmatrix}
\phi_h \\
h_0
\end{pmatrix} = H \begin{pmatrix}
\phi_h \\
h_0
\end{pmatrix}$$ (8)

If there were no nondiagonal components in the dynamic matrix, the relaxation rates are

$$\Lambda_{1,k} = \frac{\sigma \phi h_0 k^2}{3\eta}$$ (9)

$$\Lambda_{2,k} = D_k k^2 + \frac{2\phi_h - \phi^{(eq)}}{h_0}$$ (10)

which coincide with Equations (5) and (6) up to an evaporation-related contribution in Equation (10). The relaxation of perturbations in height and concentration are interrelated by the nondiagonal components of the matrix. These represent the effect of solute concentration growth, of Marangoni drag, and of vapor pressure reduction according to Raoult’s law, i.e., the reduction of solvent vapor pressure over a liquid solution with increasing solute concentration. The relaxation rates of the right eigen functions of $H$ are given by

$$\Lambda_{3,k} = \left( \frac{\Lambda_{1,k} + \Lambda_{2,k}}{2} \right) + u_c \beta \phi_h \left( u_c + \frac{h_0 k^2}{2\eta} \sigma \phi \right)$$ (11)

The parameter $\beta = \phi_h - \phi^{(eq)}$ is proportional to the thermodynamic force-driving solvent evaporation, and $h_0$ is the final thickness of the dried layer. If at least one of the two eigenvalues becomes negative, at least for some range of wave numbers $k$, undesirable pattern formation may take place instead of leveling, and will affect the liquid layer.

### 3.3. Stability Condition

It would vastly exceed space and topic of this article to discuss the various cases of relaxation and pattern formation. Instead, we briefly examine the conditions for principal stability of the liquid layer, using only the discriminant of the characteristic polynomial of the dynamical matrix in Equation (7), i.e., the expression under the square root in Equation (11). The relaxation rates are all positive, and the liquid film can be considered as stable if

$$\left( \frac{\Lambda_{1,k} + \Lambda_{2,k}}{2} \right) + u_c \beta \phi_h \left( u_c + \frac{h_0 k^2}{2\eta} \sigma \phi \right) > 0$$ (12)

This yields a polynomial relation of third order in $(h_0 k)^2$ as stability condition

$$P_k (h_0 k) = D_k k^2 + (1 + \beta) (h_0 k)^4 - \frac{3\beta \phi h_0 k^2}{2\eta} - \frac{3\beta \phi h_0 k^2}{\sigma} > 0$$ (13)

The qualitative space of stability will be discussed in the final section. The reader is invited to check out details of leveling and pattern formation rates of two-component liquid films under evaporation using the MS-Excel script provided as the Supporting Information to this article under https://tudatalib.ulb.tu-darmstadt.de/handle/tudatalib/2460.

### 3.4. Determination of Evaporation Rate and Marangoni Parameter

Some additional material parameters are required for stability analysis. The evaporation velocity $u_c$ can be determined by gravimetric measurements as already has been indicated. For practical purposes in the printing lab, it should suffice to determine the reduction of the filling level of a cup filled with the respective solvent which is exposed to a drying atmosphere that coincides with respect to air flow, temperature, and humidity to the conditions in the printing machine. Some examples, taken inside a lab flue, are shown in Table 2. The Marangoni coefficients $\sigma_q$ for a set of combinations of organic semiconductors with different solvents are shown in Table 1. If not indicated differently, sets of diluted solutions of the respective materials of 0.5, 1, 1.5, and 2 wt% have been prepared, and stirred for 1 h. As a commercially available reference to valuable small molecule semiconductors from lab-scale synthesis, printing process development also considered perylene-type fluorescent dyes such as Lumogen F 305. For the purpose of studying ink formulations and evaporation-driven pattern formation, such compounds behave sufficiently similar to the semiconductors themselves, and are available in rich variety.[35] From P3HT, it is possible to obtain two distinct solutions: an isotropic one, and a dispersion of crystalline agglomerates.[36] These samples were prepared at

| Table 2. Evaporation velocities of some common liquids at 23 °C, 50% r.h., gravimetrically determined in a lab flue. |
|-------------|---------------------------------|
| Solvent     | Evaporation velocity $u_c [10^{-9} \text{ m s}^{-1}]$ |
| Water       | 42 +/- 4                         |
| Toluene     | 441 +/- 13                       |
| 1,4-Dioxane | 417 +/- 30                       |
| Anisole     | 29 +/- 1.5                       |
| 2-Propanol  | 84 +/- 5                         |
elevated temperature of 50 °C such that the isotropic solution formed. This phase is temporarily stable when cooling the solution to ambient temperature, and surface tension can be determined. Stirring further for 24 h, we observed the agglomerate phase to form, and the measurement was repeated, yielding remarkably different values for the Marangoni drag. Surface tension of these solutions, in addition to the pure solvents, was determined by the pending drop method, using a Krüss DSA 100 measurement system. The probe space was kept under saturated solvent vapor. In view of the partly very small differences in surface tension, the influence of the density shift with increasing concentration could not be neglected.

4. Results and Discussion

4.1. Parameter Ranges of Pattern Formation versus Capillary Leveling

Figure 4 displays the positive roots of \( P_2(h_0 \phi) \) as a function of the wavelength \( \lambda = 2\pi k \) of the perturbation and the evaporation strength \( \beta \). For four different negative Marangoni parameters of \( \sigma_\phi = -0.01 \) to \(-10\) mN m\(^{-1}\). The set \( P_1(h_0 \phi) = 0 \) defines the border of the unstable domain of evaporation. It has the shape of a triangular wedge opened to the right. For other parameters, we have assumed \( D_\phi = 3 \times 10^{-11} \) m\(^2\) s\(^{-1}\), \( \sigma = 30\) mN m\(^{-1}\), \( \eta = 30\) mPa s\(^{-1}\), \( u_s = 4 \times 10^{-7}\) m s\(^{-1}\) as an example, which corresponds to the typical order of magnitude in frequently used materials. Film thickness and solute concentration were assumed to be \( h_0 = 0.5\) µm and \( \phi_0 = 0.1\) mol\%. Pattern formation is predicted inside the triangular wedge, whereas leveling of defects is possible in the outside region, i.e., for wavelengths smaller than \(\approx 20–200\) µm, or larger than few cm. Generally, the unstable range of wavelengths is wider in case of fast than for slow evaporation. On length scales below \(\approx 20\) µm, pattern formation by Marangoni drag is suppressed. This can essentially be attributed to the effect of diffusion in the liquid film which efficiently levels concentration gradients and thus Marangoni stresses on short length scales.

4.2. Pattern Formation Phenomena Specific for Gravure Printing

In principle, perturbations of any wavelength in the unstable region could grow in time, developing from microscopic, stochastic fluctuations. However, depending on printing process and parameters, perturbations are seeded on essentially two characteristic length scales: the raster width of the gravure cylinder, which is of order of 50 µm, and the viscous finger pattern originating from the fluid splitting instability in the nip between printing cylinder and substrate. The latter period is usually between 100 and 500 µm. In view of the above discussion, both are located in the unstable domain. The pattern from fluid splitting instability is usually the dominant one. Growth rates in this range of wavelengths is larger compared to the gravure raster scale. Moreover, the dominant wavelength of pattern formation induced by viscous fingering is a function of ink transfer volume and printing velocity. The ribbing pattern in the printed film appears to be the intricate result of two distinct but collaborating pattern formation phenomena: viscous finger instability in the printing nip, and an evaporation-related instability which additionally boosts the amplitude of the previous viscous finger pattern.

The lower branch at the stability border in Figure 4 could be an interesting parameter range for processing finely structured patterns of organic material, e.g., the semiconductor layer of OTFTs. The layer is stable up to wavelengths of order of

\[
\lambda_s = 2\pi h_0 \left( \frac{2D_\sigma \sigma}{3(\beta)(-\sigma_\phi)u_s h_0} \right)^{1/4}
\]

as no pattern formation should occur at \( \lambda < \lambda_s \) in spite of a negative Marangoni coefficient. It indicates that a large diffusion constant of the semiconductor in its solvent and soft drying conditions may improve the control of the printer over surface morphology of the respective layer. Negative Marangoni coefficients and large diffusion constants appear to be characteristic for solvent-based small molecule inks. In case it is not possible to shift the Marangoni coefficient to positive values by use of solvent mixtures, the aforementioned range of stability at low evaporation rates could be helpful.

For large wavelengths in the upper region of the diagram, lateral flows in the film are negligible compared to liquid evaporation into the atmosphere. The case \( \sigma_\phi > 0 \) yields unconditional stability for slow drying, i.e., for \( 0 > \beta > -1 \), as far as Marangoni drag is concerned. A comparison of printing samples showing pattern formation with spin-coated samples is highly recommended here in order to distinguish the effect from other possible mechanisms. Layer formation by spin coating is almost insensitive to the Marangoni drag. Consequently, spin coated layers from such inks should be smooth.

5. Conclusions

We emphasize that the ink parameters are not constant over the relaxation phase, but shift within progressing evaporation.
Thus, the diagram is specific for a particular instant of the evaporation process, i.e., should be recalculated continuously with decreasing film thickness $h_0$. Note that the product of layer thickness and molar solute concentration $h_0 c_0 = h$ is preserved and identical with the dry film thickness. The stability model may be confirmed by comparison with sequences of ICR images of evaporating liquid layers in the OLED process taken at different instants, i.e., liquid film thicknesses. This accessory turns out to be of great use for in-line survey in the OLED printing process, as well as in numerous other advanced printing applications. Pattern formation within the liquid can easily be identified even if the perturbation amplitude is of the order of few nm. Dominant wavelengths of pattern formation as well as the growth rates can be determined and compared with observation. Examples have been shown in already cited work.[9,14] The model supports a quantitative diagnosis of the problem. Knowing the film thickness and solute concentration where the layer becomes critical, it is possible for the printer to obtain an educated estimate on the effect of measures that could be considered in order to improve printed layer quality, in advance of further time- and resource-consuming trials. Options could be the modification of drying conditions by active air inflation, alternative solvents, or solvent mixtures in the ink formulation, or a revision of the gravure cylinder parameters, or inkjet printing parameters, respectively.

Acknowledgements

The authors acknowledge the financial support of the German Federal Department of Research and Education (BMBF) under grant no. 13N13693 (Poesie/Druckwerk).

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

functional printing, liquid interface leveling, organic light-emitting diodes, printed electronics, thin liquid films

Received: February 26, 2020
Revised: July 6, 2020
Published online: September 9, 2020

[1] J. S. Chang, A. F. Facchetti, R. Reuss, IEEE J. Emerging Sel. Top. Circuits Syst. 2017, 7, 7.
[2] G. Nisato, D. Lupo, S. Ganz, Organic and Printed Electronics, Jenny Stanford Publishing, Singapore 2016.
[3] J. Willmann, D. Stocker, E. Dörsam, Org. Electron. 2014, 15, 1631.
[4] S. D. Howison, J. A. Moriarty, J. R. Ockendon, E. L. Terrill, S. K. Wilson, J. Eng. Math. 1997, 32, 377.
[5] M. H. Eres, D. E. Weidner, L. W. Schwartz, Langmuir 1999, 15, 1859.
[6] L. Merklein, D. Daume, F. Braig, S. Schlüsse, T. Rödemeier, M. Mink, D. Kourkoulos, B. Ulber, M. Di Biase, K. Meerholz, G. Hernandez-Sosa, U. Lemmer, H. Sauer, E. Dörsam, P. Scharfer, W. Schabel, Colloids Interfaces 2019, 3, 32.
[7] S. Raupp, D. Daume, S. Tekoglu, L. Merklein, U. Lemmer, G. Hernandez-Sosa, H. M. Sauer, E. Dörsam, P. Scharfer, W. Schabel, Adv. Mater. Technol. 2017, 2, 1600230.
[8] B. Schmidt-Hansberg, M. Sanyal, M. F. G. Klein, M. Pfaff, N. Schnabel, S. Jaiser, A. Vorobiev, E. Müller, A. Colszmann, P. Scharfer, D. Gerthsen, U. Lemmer, E. Barrena, W. Schabel, ACS Nano 2011, 5, 8579.
[9] G. Hernandez-Sosa, N. Bornemann, I. Ringel, M. Agari, E. Dörsam, N. Mechau, U. Lemmer, Adv. Funct. Mater. 2013, 23, 3164.
[10] S. Khan, L. Lorenzelli, R. S. Dahiya, IEEE Sens. J. 2015, 15, 3164.
[11] E. Hrehorova, M. Rebros, A. Pekarovicova, B. Bazun, A. Ranganathan, S. Garner, G. Merz, J. Tosch, R. Boudreau, J. Disp. Technol. 2011, 7, 318.
[12] C. Bodenstein, H. M. Sauer, F. Fernandes, E. Dörsam, J. Print Media Technol. Res. 2019, 8, 19.
[13] C. Seo, D. Jang, J. Chae, S. Shin, Sci. Rep. 2017, 7, 500.
[14] M. Wegener, D. Spiehl, H. M. Sauer, F. Mikschl, X. Liu, N. Köplin, M. Schmidt, M. P. M. Jank, E. Dörsam, A. Roosjen, J. Mater. Sci. 2016, 51, 4588.
[15] K. Reuter, H. Kempa, N. Brandt, M. Bartzsch, A. C. Huebler, Prog. Org. Coat. 2007, 58, 312.
[16] D. Zelke, A. C. Hübler, U. Hahn, N. Brandt, M. Bartzsch, U. Fügmann, T. Fischer, J. Veres, S. Ogier, Appl. Phys. Lett. 2005, 87, 123508.
[17] P. G. de Gennes, Rev. Mod. Phys. 1985, 57, 827.
[18] S. Kumar, Annu. Rev. Fluid Mech. 2015, 47, 67.
[19] J. Schäfer, I. V. Roisman, H. M. Sauer, E. Dörsam, Colloids Surf. A 2019, 575, 222.
[20] L. Gao, T. J. McCarthy, Langmuir 2008, 24, 9183.
[21] N. Samid-Merzel, S. G. Lipson, D. S. Tannhauser, Phys. Rev. E 1998, 57, 2906.
[22] M. Koppe, C. J. Brabec, S. Heiml, A. Schausberger, W. Duffy, M. Heeney, I. McCulloch, Macromolecules 2009, 42, 4611.
[23] W. I. Park, D.-H. Kim, J. Jung, S. W. Hong, Z. Lin, M. Byun, Adv. Mater. Technol. 2019, 4, 1800554.
[24] S. I. Karakashew, A. V. Nguyen, R. Tsekov, Colloid J. 2013, 75, 176.
[25] T. D. Dimitrova, F. Leal-Calderon, T. D. Gurkov, B. Campbell, Langmuir 2001, 17, 8069.
[26] J. N. Israelachvili, Intermolecular and Surface Forces, Academic Press, Burlington, MA 2011.
[27] G. Reiter, Phys. Rev. Lett. 1992, 68, 75.
[28] R. Seemann, S. Herminghaus, C. Neto, S. Schlagowski, D. Podzimek, R. Konrad, H. Mantz, K. Jacobs, Rev. Mod. Phys. 2005, 77, 5267.
[29] N. Bornemann, H. M. Sauer, E. Dörsam, J. Imaging Sci. Technol. 2011, 55, 040201.
[30] I. D. Borca, M. Bestehorn, Eur. Phys. J.: Spec. Top. 2009, 166, 73.
[31] M. Bestehorn, I. D. Borca, Phys. Fluids 2010, 22, 104102.
[32] V. G. Levich, V. S. Krylov, Annu. Rev. Fluid Mech. 1969, 1, 293.
[33] N. Bornemann, E. Dörsam, Opt. Express 2013, 21, 21897.
[34] J. Stamm, D. Daume, T. Hartwig, M. Oschmann, J. Schäfer, H. M. Sauer, E. Dörsam, J. Coat. Technol. Res. 2019, 16, 1663.
[35] A. Rademacher, S. Märkle, H. Langhals, Chem. Ber. 1982, 115, 2927.
[36] W. Zhang, J. Smith, R. Hamilton, M. Heeney, J. Kirkpatrick, K. Song, S. E. Watkins, T. Anthopoulos, I. McCulloch, J. Am. Chem. Soc. 2009, 131, 10814.
[37] S. Pankalla, R. Ganesan, D. Spiehl, H. M. Sauer, E. Dörsam, M. Glesner, Org. Electron. 2013, 14, 676.