COATING AND WETTING OF SEMICONDUCTING ORGANIC AND HYBRID FILMS: FLUID-DYNAMIC PROPERTIES, PROCESS PARAMETERS, AND WETTING BEHAVIOR

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1. Introduction

Polymer based solar cells can be manufactured in a continuous roll- to- roll process as a low cost regenerative energy source. Coating ink properties and film thicknesses of 30 to 200 nm are challenging with respect to the manufacturing process, which itself has an important impact on film properties and cell efficiencies. Though a number of groups have successfully proven the principle of roll-to-roll manufacturing of PSC with a record efficiency of 3.5 %, developing a stable process for large area coating and drying with high average efficiencies and reliability is still one of the major challenges for the technology.

In this talk the implications of material properties for film formation in a continuous coating process for polymer based (semi)conductor layers are discussed. A design guideline for the selection of process parameters is presented for the slot-die coating process. Wetting of aqueous polymer inks is a major challenge for the manufacturing process and a method to optimize wetting behavior is proposed (section 2).

We present data and approximations of fluid-dynamic properties, such as viscosity and surface tension, for typical coating inks. Viscosity and surface tension can be manipulated by changing the ink composition and depend on the film temperature. The surface energies of substrates applied in polymer solar cells can be increased and adjusted by plasma treatment. We propose a model for the substrate’s surface energy increase as a function of the power and residence time of the plasma treatment (section 3).

Figure 1: Polymer based hybrid solar cell, coated on a flexible PET Substrate

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2. Process stability

A successfull film formation requires a stable coating process, which is determined by fluid-dynamic forces, and good wetting behaviour, which is determined by the surface tension and energy of ink and substrate, respectively.

2.1 High speed limit in slot-die coating

For the a slot-die coating process the limiting operating variables are the coating speed v and the wet film thickness D. The coating speed can be expressed in a dimensionless form as capillary number Ca:

$$\mathrm{Ca} = \frac{\eta v}{\sigma}, \tag{1}$$

where η is the viscosity and σ the surface tension. The inverse film thickness can be expressed in a dimensionless form as dimensionless Gap width:

$$\mathrm{G}^* = \frac{G}{D}, \tag{2}$$

where G is the distance between die lip an substrate. The resulting coating limit for semiconducting inks, determined by the equilibrium of capillary and viscous forces [1] was presented in [2] for organic solvents. Figure 2 shows additional data points for an aqueous dispersion (PEDOT:PSS, PH500, Hereaus) and a slot-die with a different lip design.

The new data is consistent with the previous results for Polystyrene (PS) in Xylene (Xyl) demonstrating that the limiting critical capillary number:

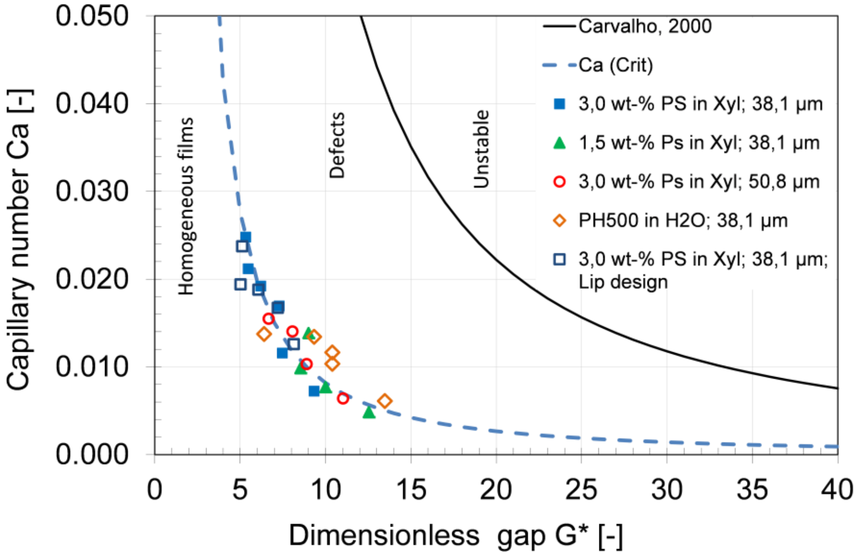

Figure 2: Critical capillary number as a function (or dimensionless coating speed) of the dimensionless coating gap (or dimensionless inverse wet film thickness).

$$\mathrm{Ca}_{Crit} = n \cdot \left(\frac{2}{G^*-1}\right)^{3/2} \qquad \text{with} \quad n = 0.0781\,, \tag{3}$$

is valid for a large number of solutions and coating parameters. For experimental details please see reference [1].

2.2 Film stability against dewetting

Especially the aqueous PEDOT:PSS layers, applied as hole injection (e.g. VPAI40.83) or electrode layers (e.g. PH500, PH1000) are challenging with respect to wetting behavior due to the high surface tension (SFT) of water. According to the theory of Owens, Wendt, Rabel, and Kaelble [3], the wetting behavior is described by polar and disperse interactions of fluid and substrate. We propose that above a critical contact angle dewetting may occur for a given viscosity and film thickness. For patterned coatings where sharp edges are required, a minimal critical contact angle may describe the point where complete spreading of the film is inhibited. These two limits define a region of optimal wetting behavior.

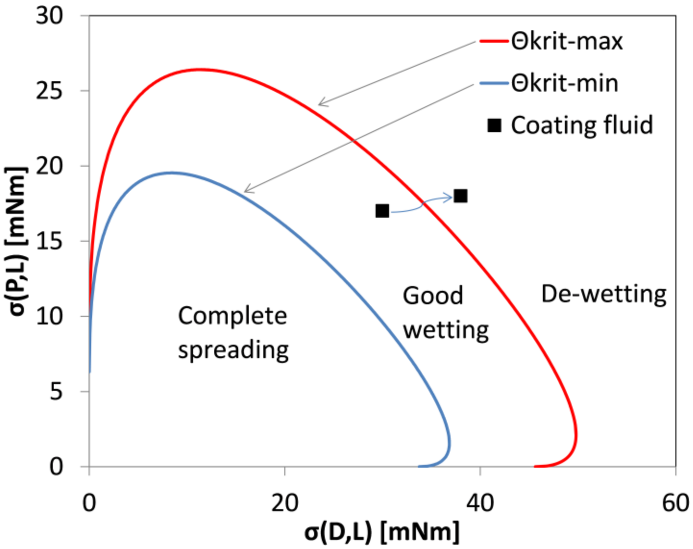

Figure 3: Schematic sketch of wetting envelopes , or lines of constant contact angle in a plot of polar vs. disperse part of the surface tension.

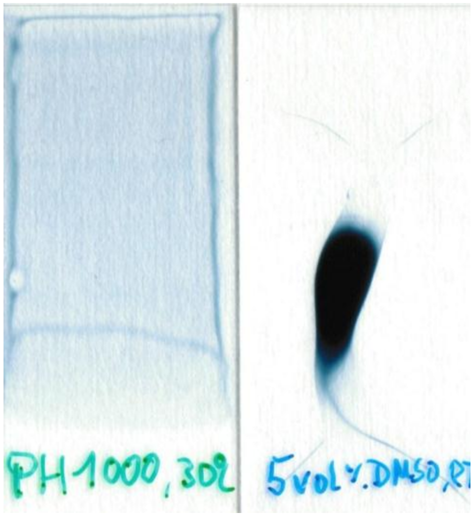

Figure 4: Scan of two PH1000 electrode films.

To validate this hypothesis, it is necessary to know the viscosity and surface tension as a function of solution composition, as these parameters may change during the drying process, indicated schematically by the arrow in Figure 3. Figure 4 shows two PH1000 films that were coated under identical process conditions but with a different initial composition. Even though both inks are initially within the Θ<0° wetting envelope, the left film shows only minor dewetting along the substrate edges, whereas the picture shows a completely dewetted substrate.

3. Material properties

Section 2 highlights the need to know fluid-dynamic properties of inks to optimize the coating and wetting process. For semiconducting films in polymer solar cells this is especially important as minor film inhomogenieties may have a strong impact on film quality. The addition of thickeners or ligands is undersireable due to the sensible functional properties of the coatings. As well, newly developed materials are available in small quantities only, an empirical approach for finding the optimized process conditions is often not feasible. We will thus present some data for material properties and review or propose methods to predict them.

The viscosity of three commercial PEDOT:PSS solutions may be described with the solid concentration, shear rate and temperature dependen model:

$$\eta_{0;20°C}(x_{Solid}) = c_1 \cdot x_{Solid}^2 + c_2 \cdot x_{Solid} + \eta_\infty \tag{4}$$

$$\eta_{20°C}(x_{Solid}, \dot{\gamma}) = \eta_{0;20°C} + (\eta_\infty - \eta_{0;20°C})\left[1 + (\lambda \cdot \dot{\gamma})^2\right]^{\frac{n-1}{2}} \tag{5}$$

$$\eta(x_{Solid}, \dot{\gamma}, T) = \eta_{20°C}(x_{Solid}, \dot{\gamma}) \cdot e^{\frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{293.14\,K}\right)} \tag{6}$$

With the parameters given in Table 1.

Table 1: Parameter values for concentration, shear rate, and temperature-dependent viscosity models. Parameters were fitted to data in the following range: xs<0.0136, 10< $\dot{\gamma}$ <10000, and 10°C<T<50°C.

PEDOT:PSS type	c_1 [mPa s/wt-%^{2}]	c_2 [mPa s/wt%]	λ [s]	n [-]	E_A/R [K]
PH100	4.064	6.351	0.0185	0.718	1205
PH500	22.24	8.308	0.054	0.688	1513
VPAI4083	-0.4166	2652	-	-	1906

The solvent viscosity is assumed to be the infinite shear viscosity and can - depending on the composition - significantly affect the overall viscosity. Data for binary alcohol- water- mixtures can be calculated by the model proposed by Gonzales, et. al. [4]. Whereas the viscosity depends on solvent composition, temperature and solid content, the surface tension of PEDOT:PSS solutions is independent of the solid content and can thus be described as a mixture of pure solvents. The temperature dependence of pure solvents is tabulated by Jasper [5] and binary interaction coefficients are given by Conors and Wright [6].

4. Summary and outlook

Starting from practical coating and wetting problems in the production of polymer based solar cells, we present a dimensionless coating window for slot-die coating that determines stable coating conditions for solvent-based photoactive films as well as aqueous electrode or hole injections layers. An optimization of wetting behavior is proposed by a minimal and maximal contact angle depending on viscosity and film thickness.

Both, coating stability and wetting behavior can only be predicted if material properties such as viscosity, surface tension, and substrate surface energy are known. We therefore discussed useful property models, and provide experimental data for substances typically applied in polymer solar cell inks.

5. References

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