Colloids and Surfaces A: Physicochem. Eng. Aspects 443 (2014) 182–187

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

# Influence of temperature on wetting properties of thin films in organic solar cells applications

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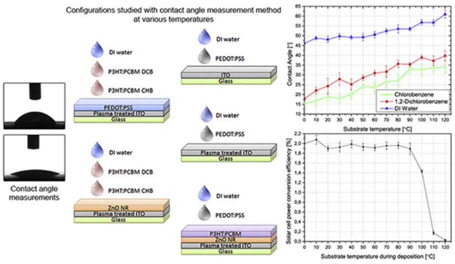
## HIGHLIGHTS

- Clear evidence that temperature could be used to manipulate the wetting properties.
- Usability studies of organic solar cell materials never investigated previously.
- Implementation of ZnO nanorod layers, which are a very promising materials for various applications.
- Proof those elevated temperatures permanently reverse the effects of plasma treatment.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 30 August 2013
Received in revised form 29 October 2013
Accepted 6 November 2013
Available online 15 November 2013

*Keywords:*
Organic solar cells
Temperature
Wetting
Contact angle
Printing
Ink-jet

## ABSTRACT

Printed electronics is a new branch of electronics that allows the development of unique devices and manufacturing methods regardless of the substrate used. Solution-processed organic solar cells are the best example of printed electronics, where the production yield can be significantly increased. While the interface between engineered ink and the substrate plays an important role in fabricating high-efficiency devices, manipulating the wetting properties of printed layers remains a challenge, as the wetting mechanism is complex and may be affected by a variety of factors. This study analyses the influence of temperature on the wettability of some popular thin-film layers used in the manufacture of organic solar cells. It tests and analyses interactions between polymer-based inks and various substrates using the contact angle measurement method. In this study, temperature was set to range between 0 and 120 °C to allow compatibility with commonly used blends and flexible substrates. Our results show that ink-substrate interactions and the consequent printing process depend on three factors: substrate temperature during processing, substrate material composition and the materials used for ink formulation. The study also indicates stable solar cell performance when manufactured with substrate temperatures below 90 °C.

## 1. Introduction

Printed electronics offers unique possibilities for the development of devices and manufacturing methods [1]. Solution-processed organic solar cells are the best example of printed electronics, where the production yield can be significantly increased. For instance, the roll-to-roll (R2R) technology made possible to print solar cells almost as fast as newspaper [2,3]. Amongst the list of printed electronic technologies, ink-jet printing promises facile implementation, selective printing and low material waste printing [4,5]. Although ink-jet is slower than gravure or screen printing, it allows implementation of new innovative capabilities, such as printing on a substrate that already has electronic structures and components. Unfortunately, ink-jet printed device

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http://dx.doi.org/10.1016/j.colsurfa.2013.11.008

performance strongly depends on the film morphology, which is affected by the behaviour of the ink at the substrate surface [6,7]. A precise control of this behaviour and consequently film morphology have been emphasized by many authors as an important factor for commercialization of printed solar cells [8,9].

The contact angle measurement is a commonly used method providing quantitative data that describes the behaviour of the ink droplet at the substrate surface. For instance, ink droplet that forms a low contact angle spreads well and distributes material over a large surface area. In contrast, the same volume droplet that forms large contact angle preserves a drop shape at the surface resulting in small area coverage but thicker layer after drying [10]. The contact angle and the volume of the ink drop are the values needed to calculate the area covered by the drop at the substrate surface and consequently to predict the printed feature size and morphology [11,12].

Ordinarily, the contact angle depends strongly on the list of inks and the confining surface properties. Some examples include: surface energy, ink formulation, surface roughness, solvent properties, processing temperature and pre/post-treatments (using heat, acid or plasma), chemical heterogeneity and many others [13,14]. Nonetheless, from the engineering viewpoint, an organic solar cell fabrication system with temperature-variation capability does not require any changes in chemical composition of either ink or substrate and therefore is easier to implement into current processing recipe.

Several groups studied the issue of dependence of contact angle and temperature and several theories have been proposed [15–23]. However, in many cases experimental results differ from proposed theoretical models. Typically, the contact angle has a decreasing trend with increasing temperature [19,18]. Nonetheless, opposite behaviour of contact angle has been also observed and reported [16,24]. For instance, Adamson's simple model described the relation between molecular surface adsorption and contact angle, where contact angle decreases with increasing temperature [22]. Contradictory, Budziak et al. suggested to consider surface entropies of solids as surface entropies of most liquids that are known to decrease with increasing temperature [16]. On the other hand, Ruckenstein and Berim proposed to utilize the density functional theory, which accounts for the inhomogeneity of the liquid density and temperatures effects for small scale systems [25]. To complicate the matter further, a certain applications, including printed solar cells, require a separate approach mostly due to the implementation of polymers and novel materials, which exhibit unique physical and chemical properties (self-assembling ability, increased surface area, etc.) with a significant effect on wettability [26–28]. To our knowledge only few reports demonstrated some links between the behaviour of various inks in correlation with the substrate temperature in the ink-jet printing applications [6,29]. Therefore a systematic evaluation of the behaviour of inks at temperature influenced substrates used in organic solar cells is needed.

This research focuses on measuring the effect of temperature on wetting of inks and substrates typically used in the organic solar cell industry. The aim is to provide a reference value describing the expected film parameters such as the spreading, at a given processing temperature. In this work four most common solutions (inks) used in organic solar cell fabrication have been investigated: poly(3-hexylthiophene-2,5-diyl):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) dissolved in 1,2-dichlorobenzene (DCB), P3HT:PCBM dissolved in chlorobenzene (CHB), poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) 4083(PEDOT:PSS) and DI water to provide a basis of comparison [30]. Furthermore, five different materials (indium tin oxide (ITO), $O_2$ plasma-treated ITO, PEDOT:PSS thin film, P3HT:PCBM thin film and ZnO nanorods (ZnO NR)) are used as substrates. To characterise the ink-substrate interface, this research employs the sessile-drop contact angle measurement method. In order to ensure the compatibility of the materials and flexible substrates, temperature was varied from 0 to 120 °C. In addition, to analyse the influence of substrate temperature on device performance, organic solar cells were fabricated for each set temperatures and their performance was examined.

**Table 1**
Properties of solvents used in the experiment.

| Chemical material | Solvent | Ratio | Concentration |
|---|---|---|---|
| P3H:PCBM | 1,2-Dichlorobenzene | 1:0.8 | $30\,\text{mg}\,\text{ml}^{-1}$ |
| P3HT:PCBM | Chlorobenzene | 1:0.8 | $30\,\text{mg}\,\text{ml}^{-1}$ |
| PEDOT:PSS 4083 | Water | | |
| DI water | NA | | |

## 2. Methods

The focus of this study was to investigate interactions between various inks and substrates at different substrate temperatures. For that reason, it applied the static sessile-drop contact-angle measurement method. These angle measurements were performed immediately after the formation of drops at the substrate, using a Kruss DSA100 system under nitrogen atmosphere. This system comes with a high speed camera (360 fps), analysis software and an environmental chamber that allows precise heating and cooling of substrates. During the experiments, substrate temperature was varied from 0 to 120 °C with 10 °C intervals and 10 min delays for temperature stabilization. To avoid gravitational flattening, drop size was limited to 1.5 μl. In addition, the chamber used nitrogen as an ambient gas to avoid the build-up of moisture on the sample surface at low temperatures. To enhance the usability of our results, conditions during contact angle testing were identical to those during solar-cell fabrication, including inert gas atmosphere, ink processing steps, layer thicknesses and type of layer beneath the investigated layer [31]. Importantly, ink materials were processed as received from Sigma–Aldrich. Contact angles were extracted using the height–width method. In this method, a contour line enclosed by a rectangle is regarded as being a segment of a circle. As a result, the contact angle can be calculated from the height–width relationship of the enclosing rectangle. The surface contact angles of droplets at three different locations on the same pre-heated sample were averaged out and standard deviations were calculated. Exact ink formulation and the examined inks-substrate configurations are presented in Table 1 and Fig. 1, respectively.

Prior to the experiment, ITO-covered glass substrates (TFD, resistivity 20 Ω/□) were solvent-cleaned (acetone, IPA, methanol) and a number of designated samples were plasma-treated with oxygen plasma for 5 min at 60 W and at an oxygen flow of 4.5 sccm. ZnO nanorods were grown using the galvanostatic deposition method, adapted from Seipel et al. [32] and D'Alkaine and Boucherit [33].

Thin films (ITO, $O_2$ plasma-treated ITO, PEDOT:PSS, and P3HT:PCBM) were analysed with Optical Profilometer (Bruker Contour GT-K) to extract their surface topology that might have influence on the wetting properties. A high scattering properties of ZnO NR makes impossible to utilize the optical method for morphology characterisation. Therefore, the ZnO NR thin film was examined with AFM (Veeco D310). Additional measurements were performed to verify the theory of temperature-accelerated deterioration of hydrophilicity as a function of aging time. A more detailed explanation of the verification steps can be found in the support material.

Lastly, organic solar cells were manufactured to verify the influence of temperature on device performance. A blend solution