

# Modeling Spray Coating of Polymer Thin Film Photovoltaic Solar Cells

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## ABSTRACT

Spraying of liquid precursors is a natural candidate for the fabrication of thin film polymer solar cells and other similar devices. Spray coating, similar to spray painting in the automotive industry, is a fast process and can be easily scaled up and be used for roll-to roll fabrication of flexible solar cells. Spray coating process is a multi-process method comprising processes such as atomization of a multicomponent liquid, droplet dynamics and flight, droplet evaporation, droplet impact on the surface, spreading, drying and adhesion of polymer molecules to one another and to the substrate. We are developing a rather comprehensive model that may be used as a design and research tool for the spray coating of solution-processed thin films. In this paper, the main modeling equations are presented.

**Keywords:** thin film solar cells, polymer solar cells, fabrication method, spray coating

## 1 INTRODUCTION

Thin films have several applications in modern technologies spanning from protective thermal barrier coatings on turbine blades to emerging technologies such as various types of thin film solar cells. To make the emerging technologies requiring thin film formation cost-effective and competitive, tremendous and vigorous research activities is being undertaken across the globe. For instance, polymer thin film solar cells have been introduced as an alternative to crystalline silicon technology. Obviously, technologies that are fast and can be easily scaled up are more favorable, demanding and practical. As such, spray coating of polymer thin film and similar solar cells is receiving considerable attention among researchers; however, the process is not adequately understood, controlled and mastered. To fabricate such thin films by spray deposition, proper coating blends such as polymer blends are dissolved in a proper solvent; the mixture or solution is then sprayed onto a substrate to form a thin film. Owing to the controllability of sprays, i.e. the possibility of producing droplets using multiple sprayers at specific droplet size and velocity, and directing them onto desired parts of the substrate in a short period of time, it is expected that the spray-coating method will permit the fabrication of

large area thin film devices such as solar cells on flexible substrates.

Spray coating process is a multiple-phenomena process comprising independent processes such as atomization of a solution or mixture liquid, droplet dynamics, droplet evaporation, droplet impact on the surface, spreading, drying and adhesion of the solid content such as the polymer blends to one another and to the substrate to form a film. While rather similar processes such as thermal spray coating and spray painting have been the subject of extensive research and development, to date, spray coating of thin film semiconductor devices and solar cells has not been sufficiently investigated and understood.

As an example, the poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methylester (PCBM) blends, a fullerene derivate based donor-acceptor copolymer, is one of the widely used organic solar cell materials (Giroto et al., 2009). PCBM, because of high hole mobility plays the role of electron acceptor in many organic cells. Organic polymers such as PH3T:PCBM blends have wider band gap than semiconductors. Thus they give an efficient absorption at near UV part. The band gap of the polymer solar cells can be altered by changing the ratio of constituents and also the arrangement and alignment of the molecules (Cook et al., 2009). Figure 1a shows the exciton dissociation at the donor-acceptor interface and Figure 1b shows a two layer heterojunction polymer photovoltaic cell. Spray coating is a viable and perhaps the best candidate to transform the above mentioned materials to a substrate and form a thin film photovoltaic solar cell.

In general, the processes involved in various types of spray deposition and coating are sometimes very different. Spray deposition for the fabrication of thin film solar cells and semiconductor devices has been recently practiced by several investigators (Ravichandran et al. 2009; Tewari and Bhattacharjee, 2011); Xu et al., 2008; Giroto et al. 2009 and 2011). Preliminary results show great potentials for the solar cell fabrication using this approach. Spray-made cells have shown a better or similar performance and conversion efficiencies compared to those cells produced by the conventional spin-coating method (Lewis et al., 2011).

The rest of this paper is organized as follows: bearing in mind that the process of thin film formation using spray deposition or spray coating has several distinct and successive steps, we present appropriate equations that can sufficiently express each phenomenon. This provides us

with a physical and mathematical model for the entire process and the governing equations.

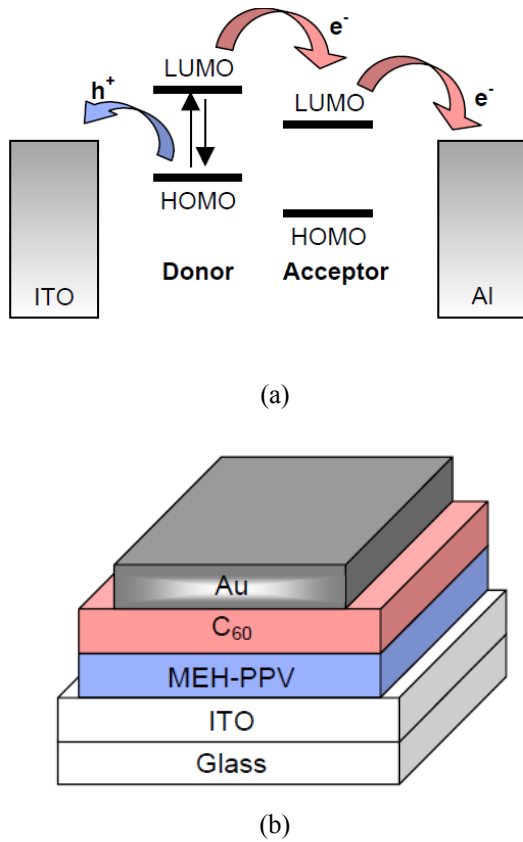


Figure 1: (a) Exciton dissociation at the donor-acceptor interface; (b) a two-layer heterojunction photovoltaic cell. HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital (Spanggaard and Krebs, 2004).

## 2 MODEL DEVELOPMENT

When a rather cold spray with low velocity droplets formed by ultrasonic atomization or similar techniques is used, there is no need for solving the gas phase transport equations. This approach is justified wherever the relative velocity between the droplets and the carrier gas is negligible, which is the case when ultrasonic atomization is used to atomize the liquid and air is used to carry the droplets to the substrate; in this case, droplet velocity is simply the same as the carrier air velocity, which can be roughly obtained from the air flow rate and mass conservation equation. Also, we note that the condition of zero relative velocity between carrier air and spray droplets will translate to a symmetric evaporation.

The other phenomenon taking place in spray coating is the droplet heating and evaporation, both during the spraying and then after drop impaction on the surface. In general, a droplet (pure liquid or solution droplet or a

droplet containing solid particles), when exposed to a relatively high temperature, experiences several heating processes starting from transient heating, evaporation (droplet temperature at the wet bulb temperature), boiling (if the gas temperature is high enough). In the case of solution droplets (polymers dissolved in a solvent), once the solvent has evaporated, a solid particle or a shell may form depending on the conditions (Eslamian et al. 2006, 2009, 2011). In the case of ultrasonic atomization used for surface coating, temperature is usually low and boiling is absent. Boiling is more concerned in a burning spray flame. In the evaporation and boiling stages, the droplet is simply losing its solvent content and shrinks. In our analysis, a symmetric evaporation is assumed and the transient heating, which is the temperature rise without evaporation, is neglected.

To ensure successful formation of a thin film, solution droplets (polymer solutions) should impinge on the substrate write before the onset of precipitation of solute on the droplet surface, to prevent the formation of a rigid shell before the impaction of the droplet.

During the shrinkage or the regressing-diameter period of a droplet, the volatile components evaporate and deplete leaving behind the solute. The droplet surface temperature depends on the ambient air temperature, humidity, and the rate of heat transfer from the surrounding air or other gases to the droplet. For low evaporation rates, droplet temperature reaches the wet bulb temperature and remains constant afterwards if the humidity does not change (Jayanthi et al., 1993; Eslamian et al., 2006). During the shrinkage period, heat is continuously transferred from the surrounding gas to the droplet. The heat or energy balance on the droplet surface, assuming that the heat transfer from the surrounding air to the droplet is only by conduction (zero relative velocity between air and droplet), leads to the following equation:

$$mc_p \frac{dT}{dt} - 4\pi Rk_g (T - T_\infty) - L \frac{dm}{dt} = 0 \quad (1)$$

where  $m$  is the mass of a droplet assuming that it is all occupied by liquid solvent,  $c_p$  is the liquid droplet heat capacity,  $T$  is the droplet temperature, which is assumed uniform within the droplet, but varying with time,  $R$  is the gas constant,  $T_\infty$  is the ambient bulk temperature,  $k_g$  is the thermal conductivity of the surrounding gas,  $L$  is heat of vaporization of liquid, and  $t$  is time. In equation (1), the heat transfer by radiation from the surrounding is not considered. Equation 1 may be used to find the droplet temperature, provided that the droplet evaporation rate can be evaluated. For droplet evaporation rate  $dm/dt$ , the following equation may be used (Jayanthi et al. 1993):

$$\frac{dm}{dt} = -4\pi R\rho_g D_g (W_{gR} - W_{g\infty}) \quad (2)$$

where  $\rho_g$  is the gas density,  $D_g$  is the gas-vapor mutual diffusion coefficient,  $W_{gR}$  and  $W_{g\infty}$  are the mass fraction of the solvent vapor on droplet surface and at infinity. Some major assumptions in derivation of equation (2) include quiescent environment, slow evaporation, local thermodynamic equilibrium on droplet surface and symmetric evaporation. The vapor mass fraction on the droplet surface may be obtained through using the Clasius-Clapeyron equation that assumed a local thermodynamic equilibrium on the droplet surface.

As seen, equations 1 and 2 are simple but coupled and transient and for each time step need to be solved simultaneously or using an iterative method. Also, if the effect of the solute wants to be considered on the vapor pressure, the Raoult's law should be considered. The following equation is deduced from Eq. (2), which is valid for micron sized droplets:

$$\left| \frac{dR^2}{dt} \right| = 2 \frac{\rho_g}{\rho_l} D_g (W_{gR} - W_{g\infty}) \quad (3)$$

$\rho_l$  is the liquid phase density. For a constant ambient humidity during evaporation, and neglecting the Kelvin effect on the saturation pressure of the droplet, the diameter-squared of the droplet varies linearly with evaporation time.

Evolution of solution droplets in the case of polymer solar cells may be explained using the concentration equation below. Considering droplet uniform temperature with no internal circulation, the equation for the spherically symmetric mass conservation of the solvent inside the droplet is as follows:

$$\frac{\partial W_l}{\partial t} - \frac{1}{\rho_l r^2} \frac{\partial}{\partial r} \left( r^2 \rho_l D_l \frac{\partial W_l}{\partial r} \right) = 0 \quad (4)$$

where  $W_l$  is the solvent mass fraction,  $r$  is the radial distance in spherical coordinate system, measured with respect to the droplet center, and  $D_l$  is the diffusion coefficient of solute in the solvent. The boundary condition at the droplet surface depends on the droplet evaporation rate, Eq. (2), making the concentration equation coupled with the gas phase evaporation rate. Details of the transformed equation and the boundary conditions are given in Eslamian et al. (2009).

With solvent evaporation, the solute concentration on the droplet surface and within the droplet increases. At the onset of precipitation, solute starts to precipitate on droplet surface, a process that leads to the formation of a shell. As the first approximation, this time is perhaps the right time for a solution droplet to arrive at the substrate. If droplets continue to shrink beyond the precipitation point, a hard shell made of polymer or other dissolved substances may

form making it difficult or impossible to spread smoothly on the substrate.

The droplet velocity at any distance from the nozzle including at the point and time of the impact on the substrate is assumed the same as the carrier gas velocity. This means that there will be no slip or relative velocity between the droplets and the carrier gas, which is valid for small droplets in a laminar flow. When the droplets emerge from the atomizer, they may accelerate (or decelerate) by the carrier gas, a phenomenon that is neglected here. In the spray coating model, initial droplet size is considered known and droplet velocity is assumed the same as the steering air velocity.

In the spray coating process, the droplets partially dry during their flight from the nozzle to the substrate, however, due to the low temperature of the carrier gas and the requirement of the process, the drying is incomplete. When the droplets land on the substrate, the drying is completed owing to the high temperature of the surface. It is important for the landing droplets to dry immediately and properly and form a solid desired structure so as to not interfere with the forthcoming droplets. Ideally, a landing droplet should dry before the next droplet arrives at the surface. Therefore, the substrate temperature should be adjusted so as to assure on-time drying of the landing droplets. Excessive substrate temperatures may result in restructuring of the structure of the film that may be beneficial or detrimental to the performance of the layer in a device.

Impaction of a droplet on a surface may lead to droplet splashing. Splashing can occur if the momentum of the droplet at the time of impact is excessive. According to Mundo et al. (1995) if  $K = Re.Oh^{1.25} < 57.7$ , the process is on the deposition mode. Obviously, in the case of thin film formation, splashing is detrimental to the quality of the film, and the operating conditions should be tuned so as to ensure that splashing is absent or negligible. And in fact since the  $Re$  associated with micron-sized droplets is small, there is literally no or little chance for splashing to occur in the case of thin film formation by ultrasonic atomization.

Drying of the landed droplets on the substrate in the case of solar cell fabrication can be considered in the category of dry-wall evaporative spray cooling mode (Grissom and Wierum, 1981). In evaporative spray cooling, the substrate temperature is greater than the droplet saturation temperature and therefore the arriving spray droplets are vaporized quickly as a result of the high temperature of the substrate. This is in fact a desired condition for the formation of various layers in thin film solar cells, i.e., the solvent content of the incoming spray should be vaporized quickly before next droplet arrives. If the surface temperature is not high enough to ensure complete vaporization of the solvent before next droplet arrives, a thin film of liquid may form in which case the evaporation mode is called the flooded mode. On the other hand, if the surface temperature is too high, the impinging

droplets on the hot surface may be deflected or bounced from the surface.

For evaporative sprays impinging on surfaces with temperatures up to the liquid boiling point, correlations have been developed for the Nu number by Oliphant et al., (1998) and Karwa et al., (2007). Below is the Karwa's correlation for the Nu number:

$$\text{Nu} = 20.344 \text{Re}^{0.659}, \quad (5)$$

where

$$\text{Nu} = hw/k \quad \text{and} \quad \text{Re} = Gw/\mu$$

$w$  being the diameter of the heated target, which is the same as the diameter of the spray at the time of impact,  $h$  the average heat transfer coefficient,  $G$  the mass flux of liquid based on the area of the targeted surface, and  $\mu$  the viscosity of the liquid. Heat transfer rate by spray cooling is much larger than that of the dry air. If in an evaporative spray cooling/boiling process air accompanies the spray droplets, effective heat transfer rate will be obtained by considering these two parallel effects. Once the combined convection heat transfer coefficient from the substrate is calculated using proper correlations, the following heat balanced equation may be used to estimate the time required for the evaporation of residual solvent in the film:

$$q = hA(T_s - T_\infty) = N \frac{dm_r}{dt_r} h_{fg} \quad (6)$$

where  $A$  is the spray cross sectional area on the substrate and  $m_r$  is the residual solvent. Above equations may be used as a design tool to design proper experiments.

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