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# MORPHOLOGY DEPENDENT SHORT CIRCUIT CURRENT IN BULK HETEROJUNCTION SOLAR CELL

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## ABSTRACT

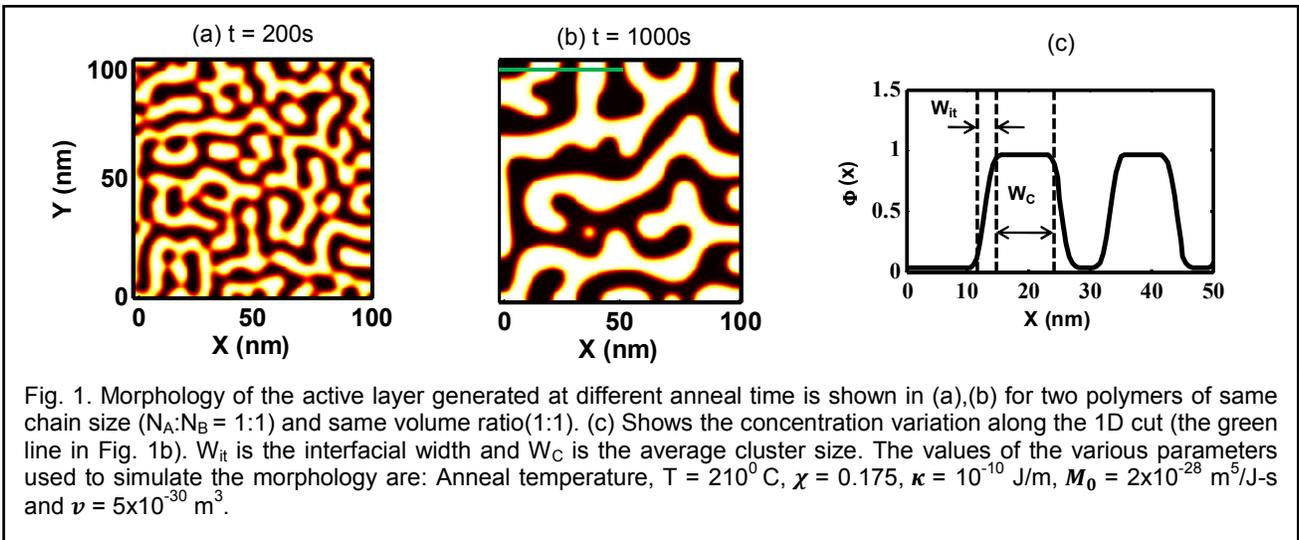
Polymer based bulk heterostructure (BH) solar cell offers a relatively inexpensive option for the future solar cell technology, provided its efficiency increases beyond the current limit of 4-6%. In this paper we propose a novel theoretical/computational process/device simulation model of organic solar cell and thereby quantitatively and explicitly relate (possibly for the first time) the process conditions to the solar cell performance. We find that the maximum limit of short-circuit current ( $J_{SC}$ ) follows a simple power law with the anneal time ( $J_{SC} \propto t_a^{-n}$ ), for  $t_a \geq t_{a,opt}$ , and we determine the optimum anneal time ( $t_{a,opt}$ ) considering exciton dissociation ( $t_{hj}$ ) and percolating pathway formation for charge carriers ( $t_{prc}$ ). Our results anticipate experimentally observed trends and have obvious and significant implications for the determination of performance limit and the optimization of the BH solar cell.

## INTRODUCTION

Bulk heterostructure (BH) promises to improve efficiency [1, 2] of organic solar cells by making the distributed donor-acceptor junctions accessible within the diffusion length of the light-induced excitons, thereby enabling exciton separation into useful electron-hole pairs before they can disappear through self-recombination. Thus the structural complexity of the active layer morphology is the necessity for the efficient operation of the cell. However, due to this structural randomness, BH solar cell requires a completely different approach for the modeling of the I-V characteristics of the cell. Since the

performance of the cell is intimately dictated by the active layer morphology, hence without a proper quantitative description of it, any further analysis like optical absorption or electron/hole pair transport is practically irrelevant for the BH type solar cell. In sum, modeling the active layer morphology as a function of process variables sets up a simulation framework which is not only appropriate for the further description of the coupled exciton/electron/hole flow in the disordered polymer network, but also guarantees to connect the process variables to the ultimate device performance.

There are significant empirical evidences [3-6] that the structural randomness in the morphology emerges due to the phase segregation process during the fabrication of the cell. In this paper, we model this phase separation process by free energy approach and we solve the Cahn-Hilliard equation [7] for the simulation of the evolution of morphology with anneal time. In Fig. 1(a, b) we show the simulated structure of the active layer with the geometrical details shown by 1D cut in Fig. 1(c). In practice, the phase-segregation that allows the morphology to evolve (from Fig. 1(a) to 1(b), for example) is achieved by various means [8], e.g., in the widely used P3HT/PCBM solar cells, some use slow-drying of spin-coated films, others anneal a homogenized blend at moderate temperature for a time  $t_a$ , and still others prefer vapor annealing. Regardless the approach, the process kinetics appears complex and final structure is randomly interpenetrating clusters of polymer and fullerene, with no discernable periodicity. During subsequent optoelectronic operation, photons are absorbed in one or both the



<p>Process Model:</p> $\frac{\partial \phi}{\partial t} = M_0 \left( \nabla^2 \frac{\partial f}{\partial \phi} - 2\kappa \nabla^4 \phi \right) \dots \dots (2)$ $f = \frac{k_B T}{v^3} \left[ \frac{\phi \ln(\phi)}{N_A} + \frac{(1-\phi) \ln(1-\phi)}{N_B} + \chi \phi(1-\phi) \right] \dots (3)$ $W_C \sim [M_0 f'' \sqrt{\kappa \Delta f} t_a]^n \dots \dots (4)$	<p>Fig. 2. Eq. 2 is the Cahn-Hilliard eq. used to simulate kinetics of phase separation and Eq. 3 is the free energy density function for the polymer mixture used for simulation. <math>\phi</math> is the volume fraction of one of the polymers, <math>M_0</math> is a positive transport coefficient, <math>\kappa</math> is gradient energy coefficient, <math>\chi</math> is the Flory interaction parameter for the 2 polymers, <math>v</math> is the volume of a single monomer unit and <math>N_A, N_B</math> are polymer chain lengths. Eq. 4 is the Lifshitz-Slyozov law describing how domain size gets larger with anneal time. Eq. 5 is exciton diffusion equation where <math>G_{ex}</math> is the effective exciton generation rate, <math>n_{ex}</math> is exciton concentration. Eq. 6 states volume conservation where <math>T_{film}</math> is the thickness of the active layer and <math>\eta_A</math> is the volume-fraction of phase A (e.g., for 1:1 blend, <math>\eta_A = 0.5</math>) Eq. 7 is the analytical model for <math>J_{SC}(\max)</math>, where <math>\alpha_s</math> is the shape factor (<math>2 \leq \alpha_s \leq 4</math>) Eq. 8 shows the minimum anneal time required for heterojunction formation.</p>
<p>Device Model:</p> $\frac{\partial n_{ex}}{\partial t} = D_{ex} \nabla^2 n_{ex} - \frac{n_{ex}}{\tau_{ex}} + G_{ex} \dots \dots (5)$ $L_A(t_a) \times W_C(t_a) \times T_{film} = \eta_A \times V = constant \dots (6)$ $J_{SC} = \alpha_s \frac{\eta_A G_{ex} L_{ex} T_{film}}{W_C(t_a)} \sim t_a^{-n} \text{ for } W_C \gg L_{ex} \dots (7)$ $t_{hj} \propto \kappa / M(f'')^2 \dots (8)$	

phases of this phase-separated quasi-random polymer blend to produce charge-neutral excitons. These excitons must then diffuse to the interfacial boundary of the polymer and fullerene to be separated into electrons and holes, before being transported to the respective electrodes to contribute to the output current. If the interface is too far away from the point of generation of exciton (domain size  $W_C \gg \sqrt{D_{ex} \tau_{ex}}$ ), a significant fraction of the excitons would be lost due to self-recombination. On the other hand, too small domain size ( $W_C \ll \sqrt{D_{ex} \tau_{ex}}$ ), leads to diffused heterojunction ( $W_{int}$  will be large, see Fig. 1c), with quasi electric field at the junction not sufficiently strong to dissociate excitons *and exciton dissociation rate would be very weak*. Finally, even if the excitons are separated with 100% efficiency with  $W_C \sim \sqrt{D_{ex} \tau_{ex}} \ll T_{film}$ , where  $T_{film}$  is the film thickness, a significant fraction of dissociated electron-holes would then be trapped in isolated or wrongly connected islands (Fig. 1a), with loss in  $J_{SC}$  and fluctuations in open circuit voltage,  $V_{oc}$ . Longer annealing connects previously isolated islands to the electrodes and increases the 'useful volume fraction  $U_{vol}$ ' (defined as the fraction of the total volume connected to the appropriate contact for collection of electrons and holes, respectively) but resulting coarser morphology degrades exciton collection. *In sum, three morphology dependent factors:  $W_C$ ,  $W_{int}$  and  $U_{vol}$  connects morphology to the efficiency of the solar cell.*

Given the complexity of process kinetics and electrical response, it is hardly surprising that most studies in the literature make no explicit effort to model the morphology to predict device performance. Some groups focus exclusively on process models [9, 10]; others, instead, describe the electronic transport in the polymer blend via an effective media approach[11] and solve the transport equation in a homogenized material. Given the scale of phase separation in typical samples, this approach does not lead to a morphology-aware predictive model, because the macroscopic mean-field diffusion constant ( $D_{eff}$ ) and mobility ( $\mu_{eff}$ ) extracted from experimental data depends on the morphology of the film

itself. In short, transport in this meso-structured, phase separated donor/acceptor BH is a nontrivial, multifaceted optimization problem which is not readily amenable to classical analysis, and as such, it still unclear from theoretical perspective what improvement in process conditions, if any, could enhance efficiency of the cell.

In this paper we present a simple analytical model for the short circuit current,  $J_{SC}$ , that explicitly captures some subtle features of exciton transport in the meso-structured geometry and thereby quantitatively relate – possibly for the first time -- the process conditions to the solar cell performance. In sum, our model predicts that for thin-film bulk heterostructure solar cell, short circuit current ( $J_{SC}$ ) is related to the annealing time ( $t_a$ ) through a simple scaling law, i.e,

$$J_{SC} \propto t_a^{-n}; \text{ for } t_a \geq t_{a,opt} = \max(t_{prc}, t_{hj}) \quad (1)$$

where  $0.2 \leq n \leq 0.33$ ,  $t_{prc}$  is the minimum anneal time required for 100% percolated network ( $U_{vol} \sim 1$ ) and  $t_{hj}$  is the minimum anneal time required to form a sharp enough heterojunction sufficient to dissociate exciton. The formula suggests that the window of opportunity for improving efficiency is rapidly lost with increasing annealing time. Below we first provide a simple analytical derivation of the Eq. (1) and support the formula via detailed numerical simulation of the spatially-resolved time-dependent exciton transport problem in a spinodally phase-separated polymer blend.

## PROCESS MODEL

It is well accepted that phase separation of the donor and the acceptor polymer is the key process which dictates the final morphology and this phase segregation is readily modeled within the framework of Flory-Huggins mean field theory [7]. According to this theory, phase separation process between a pair of polymers depends on the free energy function,  $f$ , which consists of two

primary terms: one corresponds to the entropy of mixing, which wants to keep the mixture in the homogeneous/mixed form and the other term is for enthalpy (or the interaction energy) of formation describing the tendency of the mixture to get phase segregated. Mathematically, the free energy function for the mixing between the D/A polymers is described by eq. (3) in Fig. 3. However, the evolution of the active layer morphology with anneal time depends upon the kinetics of the polymer-polymer phase separation process, which is generally described by the well-known and broadly validated Cahn-Hilliard (C-H) equation [12, 13] (Eq. 2 in fig. 2). C-H equation evaluates the local composition ( $\phi(x, y, t)$ ) change with anneal time based on the minimization of the total free energy. The first term on the right hand side of the equation is diffusive with diffusion coefficient depending on the free energy change. The second term accounts for the surface tension effect due to the formation of the diffused interface. Despite its phenomenological nature, the C-H equation with appropriate parameterization anticipates wide range of phenomena including spinodal phase-segregation, nanoparticle dispersion, Oswald ripening, fractionation of polymers with solvent concentration, etc. The phenomenological constants of the C-H model (see caption of Fig. 1) are determined by comparing the numerical simulation for typical cluster-sizes with the corresponding experimental values reported for a P3HT and PCBM (1:1) blends in Chlorobenzene solution. Typical 2D simulation results for the phase separated geometry for the anneal temperature 150<sup>o</sup> C and two different anneal times are shown in Fig. 1a ( $t_a=200$  sec) and 1b ( $t_a=1000$  sec), respectively. Indeed, Ref. [14] provides a beautiful experimental confirmation of this blend-dependent morphology anticipated by the C–H equation.

Even though the meso-structure so generated lacks any specific order/shape, it has a characteristic average domain width  $W_C$  (refer Fig. 1(c)) that increases systematically with anneal time  $t_a$ . The growth of domain size with anneal time is due to the phenomena called Oswald ripening. The main idea behind Oswald ripening is to reduce the interfacial area for minimizing the total free energy of the system. We plot the average domain size  $W_C(t_a)$  as a function of anneal time in Fig. 3(a) and the figure shows that  $W_C(t_a)$  follows a power law with anneal time that stabilizes with constant power-exponent with minutes of the initiation of the phase separation. This power law is derived in literature by Lifshitz and Slyozov and is known as Lifshitz-Slyozov law [15] (Eq. (4)). Experimentally, the characteristic length scale of  $W_C$  is interpreted as the inverse of the peak-vector ( $q_{max}$ ) from the light-scattering experiments, i.e.  $W_C \sim 2\pi/q_{max}$  and measurements of polymer blends confirm the robustness of the power-law<sup>18</sup>. We reproduce this power-law in Fig. 3c to validate the numerical implementation of our model.

## DEVICE MODEL

When photons are absorbed in this meso-structured system, they generate charge-neutral excitons in polymer (P3HT). Only a fraction of excitons so generated can reach the P3HT/fullerene distributed boundary (or charge separating zone) before being lost to self-recombination. The diffusion of the excitons towards the interfacial boundary is described by the continuity equation (5) *within* the phase segregated geometry. Given the phase-separated structure of the polymer blends, one can solve continuity equation numerically but the analytical solution of Eq. (2) on the random geometry has generally been considered highly difficult.

The problem becomes accessible to analytical solution if we recognize that for exciton dissociation, the shape of entire morphology is not very important. The only thing that is crucial in exciton dissociation is the presence of the interface within a diffusion length of the photo-generated exciton. Therefore, for the analytical solution of exciton transport, it is appropriate to transform the complicated phase segregated geometry into a simpler regularized structure while keeping the integrated volume of the two phases conserved (Eq. (6)) because inter conversion between the phases are prohibited. Moreover, the width of the transformed geometry needs to be same as that of the average cluster width,  $W_C$ . Geometrically, this type of transform can be justified if we note that after the early stage of phase separation, the fractal-dimension [16] of the structure remains close to the geometric dimension and as such there is only one predominant characteristic average domain size  $W_C$ . Now, if we envision phase A as an effective rectangle with length  $L_A$  and width  $W_C$ , *assuming perfect exciton dissociation at the interface*, it is easy to see that only the fraction of excitons generated within the distance  $L_{ex} = \sqrt{D_{ex}\tau_{ex}}$  from the interface would be charge separated into useful electron-hole pairs. Therefore, neglecting any further loss of charge carriers, the expression for the short circuit current can be given by Eq. (7).

To assess the validity of Eq. (7), we *numerically* generate a series of phase-segregated polymer blends with various annealing times, discretize the complex meso-structure for carrier transport, and numerically solve the exciton diffusion equation (with microscopic diffusion coefficient) by finite volume method with the boundary conditions that excitons dissociate fully at the hetero-interface. The results from detailed numerical simulation are plotted in Fig. 3c (dashed lines) and they show remarkable agreement with the analytical model (solid line,  $\alpha_s = 2.1$ ), suggesting that simple power-law does capture the essence of the transport problem and that any fluctuation in  $W_C$  are averaged over by the dynamics of diffusion process. Moreover, the solid circles in the figure are the experimental data points (scaled by a constant factor) showing that the simulation results correctly capture experimental trends in  $J_{SC}$ .

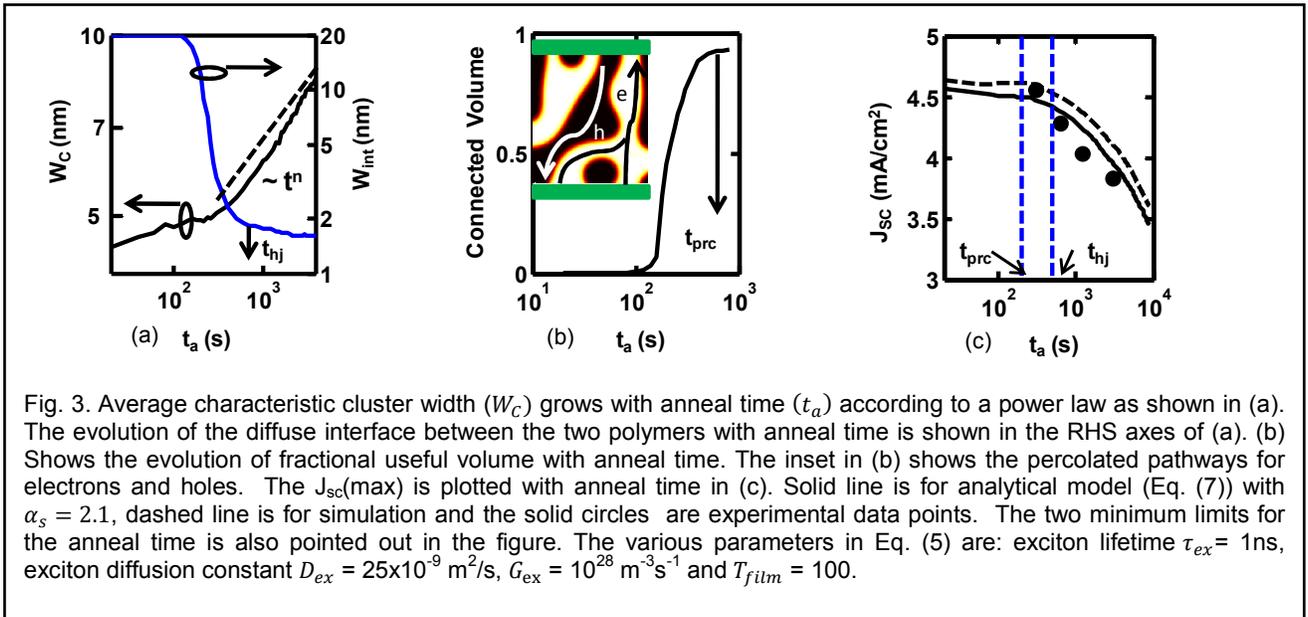
## DISCUSSION

The power law in the expression of  $J_{SC}$  with anneal time (Eq. (7) in Fig. 2) does not capture the full story of solar cell performance, because it suggests that even at the early stage of device fabrication annealing is counterproductive (annealing reduces  $J_{SC}$ ), contradicting extensive empirical evidences [6, 17-19]. Consideration of two additional counterbalancing factors – one related to exciton dissociation efficiency (related to interface width  $W_{int}$ ) at the distributed BH junction and the other due to collection efficiency (related to connected volume  $U_{vol}$ ) by the contacts – resolves this dilemma.

At very early stage of the phase separation process, the heterojunctions are not well defined ( $W_{int}$  in Fig. 1c will be very large as plotted in Fig. 3(a)). Therefore, even if the excitons reach the interface, the interface electric field (effective electric field) is too weak to dissociate exciton into e/h pairs. Given  $W_{int}(t_a)$  in Fig. 1c and assuming that electric field,  $E = (\chi_A - \chi_D)/W_{int}(t_a)$ , ( $\chi_A$  and  $\chi_D$  being the electron affinities of acceptor and donor phase), the Onsager theory suggests that for efficient charge transfer, the effective width ( $W_{int}$ ) of the interface (refer to Fig. 1(c)) should be close to its minimum/saturation value. In Fig. 3(a) we have shown the anneal time dependent evolution of the interface, and the figure clearly shows that after a certain duration of annealing, the interface width saturates to its minimum value ( $W_{int}(min) \sim 1.5$  nm). The minimum anneal duration required for the interface formation is denoted as  $t_{hj}$  in the figure and we name this anneal duration as heterojunction formation time ( $t_{hj}$ ). This minimum anneal duration  $t_{hj}$  not only indicates the sharp interface formation, but also points to the completion of the early stage of phase segregation process. For annealing beyond  $t_{hj}$ , the individual domains of the donor/acceptor phases will grow bigger just like Ostwald ripening. Thus,  $t_{hj}$  can also be interpreted as the incubation period for the phase segregation process. Both the terms: minimum interface width ( $W_{int}(min)$ ) and the corresponding

minimum anneal duration ( $t_{hj}$ ), are material dependent constants and can be derived analytically as a function of the properties of donor/acceptor polymers as shown in eq. (8) in Fig. 2. In the OPV literature, we do not find any discussion about this heterojunction formation time ( $t_{hj}$ ) because during solvent evaporation phase of the fabrication process itself the interface becomes abrupt enough that no additional annealing is required for the improvement of charge transfer process. However, for some other polymer system (other than P3HT/PCBM), additional processing may be important for sharpening the interface. Thus,  $t_{hj}$  sets up a constraint on the minimum anneal time which is essential for sharp interface formation and hence efficient charge transfer.

The generated electron/holes, however, cannot be collected by the contacts unless there exist continuous percolating pathways[20, 21] for electron and holes (inset of Fig. 3b). It is clearly visible in Fig. 1(a) that, at the initial phase of annealing the active layer contains lot of floating islands, which cannot contribute to the output current. However, as we anneal the sample for longer duration, the floating islands grow bigger, connect themselves, and ultimately form percolating pathways from the anode to cathode. So to maximize the output current, the processing of the active layer need to be carried out in such a way that, the major fraction of the total volume of both the phases gets connected to the respective contacts (Donor phase should be connected to anode and acceptor phase to cathode). Here we define two quantities  $U_{vol-A}$  and  $U_{vol-D}$  as the fraction of the total acceptor phase volume and donor phase volume respectively, connected to the appropriate contact. Depending on the initial blending ratio of acceptor and donor polymer molecules,  $U_{vol-A}$  and  $U_{vol-D}$  will be different and the smaller of the two, denoted as  $U_{vol}$ , dictates effective percolated transport. Now, the process simulation shows that  $U_{vol}$  gradually increases with anneal time as revealed in Fig. 3(b), demonstrating how longer annealing improves carrier transport. This constraint for carrier transport due to the effect of 'connected volume' sets another lower bound



for the optimum anneal time which we call percolation time ( $t_{prc}$ ). We have already discussed about minimum anneal time requirement for the formation of heterojunction ( $t_{hj}$ ). Hence, the optimum anneal time is approximately equal to the larger of these two time constraints-  $t_{prc}$  and  $t_{hj}$ , i.e.

$$t_a(opt) \sim \max(t_{prc}, t_{hj})$$

### CONCLUSION

In sum, we have developed a simple scaling- law for short circuit current in BH solar cells and validated the model by numerical solution of exciton diffusion equation in the spinodally phase-segregated morphology defined by the Cahn-Hilliard equation. The model explains the dependency of short circuit current on process parameters like anneal temperature, anneal duration, blending ratio and polymer details like chain lengths and volume of the polymer molecules etc and demonstrates how the parameters must be optimized for improved efficiency of the cell. Finally, our results regarding useful area function explains the puzzle of how it is possible to achieve close to 100% quantum efficiency in such disordered BH cells.

### ACKNOWLEDGEMENT

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