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Modeling and Optimization of Polymer based Bulk Heterojunction (BH) Solar cell

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Abstract
A polymer phase separation model based on Cahn-Hilliard equation and a three-dimensional (3D) coupled exciton/electron/hole transport model in the disordered, phase-segregated morphology so generated, allow us to predict– possibly for the first time – the morphology dependent performance limits of polymer/fullerene bulk heterostructure (BH) solar cells. We relate the optimum anneal time to polymer sizes, solvent content, film thickness, and anneal temperature and find that a regularization of the morphology can double the efficiency of BH cells.

1. Introduction
Polymer based organic solar cell remains an intriguing technology option for its promise of low cost, large scale, roll-to-roll manufacture. For economic viability, however, the low-process cost needs to be complemented by more than 50 % improvement in efficiency $\eta$ (currently pegged at ~ 3-6% [1]). Such dramatic improvement in $\eta$ must necessarily rely on theoretical models that can translate the characteristic, irreducible complexity of the process/devices of organic cells to achievable efficiency.

The cartoon of a BH solar cell in Fig. 1a illustrates four key processes that dictate its efficiency, i.e., exciton generation rate ($G_{ex}$), exciton diffusion ($D_{ex}$) and dissociation at the donor/acceptor interface, and the collection of electrons and holes in their respective contacts. These processes are often encapsulated in simple rate equation models to relate the effective material parameters to the efficiency of the cell [2, 3, 4]. However, the most modern versions of rate equations do not adequately capture the fundamental innovation of BH cells: With $L_{ex} = \sqrt{D_{ex} \tau_{ex}} \approx (10 - 20) \text{nm}$, acceptable efficiency is achieved only if the donor-acceptor (D-A) polymer blends are spinodally phase-segregated (Fig. 1b) via annealing, so that a photo-excited exciton would find a D-A surface within $\sim L_{ex}$ regardless the point of its generation. Obviously the performance of the solar cell is intimately dictated by this morphology and yet we know of no model in the literature that explicitly relates the meso-structure of the phases to the efficiency of the solar cell.

In this paper, we present a theoretical/computational process/device model of polymer/fullerene solar cells to explore the coupled flow of exciton/electron/hole within the meso-structure of the cell and quantitatively relate -- possibly for the first time -- the process conditions to the performance of BH solar cell. Moreover, 3D process/device simulation results explicitly predict an optimum annealing time as well as optimum film thickness (section 2 & 3). Finally, we

![Fig. 1. (a) Schematic of donor acceptor BHJ solar cell. Dark material is fullerene and the yellow indicates polymer. Excitons (e-h pair denoted as red and white dot), generated in polymer, charge separates at the interface. (b) 3D view of simulated phase segregated morphology on a 100x100x40 grid. (c) Free energy density function for the polymer-fullerene pair. A phase of initial composition $\phi_0$ separates into two phases $\phi_A$ and $\phi_B$, thus lowering the free energy from $f_0$ to $f_{sep}$. (d) The typical phase diagram shown for the polymer fullerene system. Above the critical temperature $T_c$, there will be no phase separation. Below $T_c$ phase separation takes place by spinodal decomposition or nucleation and growth depending on initial conc.](image-url)
Exciton Diffusion:

Process Model:

\[
\frac{\partial \phi}{\partial t} = M_0 (\nabla^2 \phi + 2\kappa \nabla \phi) \quad \ldots \ldots (2)
\]

\[
f = k_B T \frac{(1-\phi) \ln(1-\phi)}{N_A} + \frac{(1-\phi) \ln(1-\phi)}{N_B} + \chi(1-\phi) \quad \ldots \ldots (3)
\]

Electron/Hole Transport:

\[
D_{e/h} \nabla^2 n_{e/h} - \frac{n_{e/h}}{\tau_{e/h}} + G_{e-h} = 0 \quad \ldots \ldots (5)
\]

Fig. 2. Eq. 1 shows the entropy and enthalpy contribution in the free energy of the mixture. 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 [5]. \( \phi \) is the volume fraction of one of the polymers, \( M_0 \) is a positive transport coefficient, \( \kappa \) is gradient energy coefficient, \( \chi \) is the Flory interaction parameter for the 2 polymers, \( v \) is the volume of a single monomer unit and \( N_A, N_B \) are polymer chain lengths. Eq. 4 is exciton diffusion equation where \( G_{e-h} \) is the effective exciton generation rate at the surface and \( \alpha \) is the photon absorption coefficient. We use diffusion equation (Eq. 5) for carrier transport with the e-h generation term obtained from the solution of exciton diffusion (Eq. 4).

2. Process Model

We use the well-known and broadly validated Cahn-Hilliard (C-H) equation [6] (Eq. 2, Fig. 2) to describe the spinodal phase separation as a function of anneal time, \( t_a \). The driving forces of the spinodal phase separation are the competition between entropy of mixing polymers of lengths \( N_A \) and \( N_B \), and the interaction energy between the material pairs (given by Flory parameter \( \chi \) ) and both the factors can be quantitatively expressed through the free energy density function (Eq. 3, Fig. 2) . The kinetic part of the process (as given by C-H equation) depends on the interfacial energy (given by gradient energy coefficient \( \kappa \)), and effective diffusion parameter \( M_0 \) (dictated by solvent, e.g. Chlorobenzene or Toluene), and these parameters dictate how quickly the mixture eventually settles to the minima of the free energy curve (Fig. 1c). Fig. 1d shows the evolution of the phase segregated BH active layer morphology with \( t_a \). Even though the meso-structure lacks any specific order, but it is characterized by an average domain width \( W(t_a) \) which scales via the Lifshitz-Slyozov law [7] i.e. \( W(t_a) \sim \left[ D_{eff} \cdot t_a \right]^n \) with \( n \sim 1/3 \). We reproduce this power-law in Fig. 3d to validate the numerical implementation of our model.

3. Device Modeling and Optimization

Given the morphology at a particular \( t_a \) only a fraction of the photo-excited charge-neutral excitons can diffuse to the polymer/fullerene distributed boundary (or charge separating zone) before being lost to bulk self-recombination. We numerically solve the 3D exciton diffusion equation (Eq. 4, Fig. 2) within this phase-segregated geometry – thereby relating the exciton flux \( J_{ex} \) to the (anneal-time dependent) morphology of the film. Fig. 4 shows the solution of time dependent exciton diffusion on the phase segregated geometry (corresponding to a given \( t_a \), once the light source is removed at time \( t = 0 \). We also calculate the steady state total exciton flux \( J_{ex} \) \( (t = \infty) \) per unit area of the interfacial region on the morphologies generated at different anneal times and it is plotted in Fig. 5a. Assuming that all the

Fig. 3. (a), (b), (c) are the 2D X-Y cut for the same 3D morphology at different anneal times. We observe a characteristic cluster size \( W \), as shown in (c), in each of these morphology which grows with anneal time. The various simulation parameters are: \( M_0 = 1.1 \times 10^{-32} \) cm⁷/l-s; \( \kappa = 10^5 \) J/cm, \( N_A = 40, N_B = 10 \) Volume of single monomer unit \( (v) = 5.23 \times 10^{-28} \) m³. (d) Characteristic cluster size growth as a function of anneal time shows a power law dependence \( W \sim t_a^n \), where \( n \sim (\frac{4}{3}) \). This power law validates the numerical implementation of the spinodal phase separation of polymer-fullerene system.
excitons that come to the interfacial region dissociates into electron hole pairs and all the dissociated electron hole pairs can reach the respective electrodes, the maximum limit for the short circuit current density ($J_{\text{SC}}$) is estimated and is shown in Fig. 5a. as a function of anneal time.

Once excitons are charge separated, electrons/holes are transported to the anode (Al electrode)/cathode (ITO) through the percolating pathway provided by the polymer (fullerene) clusters. Figs. 5b and 5c show, however, that only a fraction of the polymer (or fullerene) volume is connected to the correct electrode for electron collection and the carriers are prevented from exiting through the wrong contact by appropriate blocking layers [8]. Moreover, floating islands do not contribute to output current. Obviously, the connectivity increases with anneal time (Fig. 5c), as the width of the phase-segregated region scales as $W \sim t_a^n$ (Fig. 3d). However, Fig. 5b already indicates that $J_{\text{ex}}$ decreases rapidly with $t_a$. These two counter-balancing trends results in an optimum anneal time ($t_{\text{opt}}$) for maximum Short circuit current, $J_{\text{SC}}$, of solar cell (see Figs. 6a and 6b). This optimum value of the anneal time ($t_{\text{opt}}$) monotonically increases with the thickness of film as shown in Fig. 6c. Moreover, the maximum value of short circuit current ($J_{\text{SC}}$) at optimal annealing increases with film thickness as more and more photons are absorbed (Fig. 6c), but beyond the photon absorption length, the geminate recombination (cross marks in Fig. 5b) [9] ensures that no further improvement in $J_{\text{SC}}$ is possible.

### 4. Regular Structure

Finally, it is natural to ask if efficiency can be improved by regularizing the morphology [10]. Fig. 7a. shows a well ordered 3D regular finger structure with columns of fullerene (dark) and polymer (bright). Unlike the phase-segregated BH cell discussed above, there are no floating islands in this structure. The 3D simulation for exciton diffusion (Fig. 7b) shows that random morphology may be better for exciton dissociation due to its larger interfacial area but there is more than factor of 2 improvement [11] in overall $J_{\text{SC}}$ (Fig. 7c) for regular structure due to its better e-h transport properties.
We have demonstrated for the first time the possibility to complement the empirical approach to polymer solar cell design by predictive theoretical models of spinodal decomposition and exciton/electron/hole transport for designing better experiments and improved efficiency. We conclude that (i) there is an optimal anneal-time (Figs. 6a & 6b) and film thickness (Fig. 6c) for BH solar cells that is uniquely defined by the polymer blends of the cell, and that (ii) regularized structure like double-gyroids or stampled structures may offer more than 100% improvement (Fig. 7c) in efficiency to justify the additional processing cost.

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5. Conclusion

We have demonstrated for the first time the possibility to complement the empirical approach to polymer solar cell design by predictive theoretical models of spinodal decomposition and exciton/electron/hole transport for designing better experiments and improved efficiency. We conclude that (i) there is an optimal anneal-time (Figs. 6a & 6b) and film thickness (Fig. 6c) for BH solar cells that is uniquely defined by the polymer blends of the cell, and that (ii) regularized structure like double-gyroids or stampled structures may offer more than 100% improvement (Fig. 7c) in efficiency to justify the additional processing cost.

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