Organic Solar - Organic Solar Cell Simulation and Tuning with Optimizer

In recent times there has been considerable interest in the use of organic materials in display technologies. Recognition of the benefits of inexpensive materials and processing as well as large area conformal construction have also placed high interest in organic solutions for solar energy applications. Silvaco has long been a leading supplier of organic simulation tools for organic light emitting devices, OLEDs, and organic thin film transistors, OTFTs, as well as crystalline solar cell simulation in general. Recently, Silvaco has released a product addressing the simulation needs of the organic solar cell technologists. This product, aptly named Organic Solar, is described in this article.

Organic Solar models bulk heterojunction (BHJ) organic solar cells using the approach of Korster et al. (1) This model can be described as follows. BHJ solar cells consist of an interpenetrating mixture of donor and acceptor materials. Absorbed light generates excess excitons which are charge neutral and diffuse to the acceptor-donor interface where they dissociate into free electron-hole pairs. The electron-hole pairs are then separated by the internal field and are swept up at the contacts as in crystalline photodetectors.

The model includes the standard drift-diffusion equations (Poisson's equation and the electron and hole continuity equations) augmented by the singlet exciton continuity equation:

$$\frac{ds}{dt} = G_{ph} - \texttt{KNRS.EXCITONS} \cdot S - R_D np + R_L np$$

where S is the singlet concentration, G_{ph} is the photogeneration rate, $\texttt{KNRS.EXCITON}$ is the non-radiative singlet decay rate, $R_D np$ is the exciton dissociation rate and $R_L np$ is the Langevin recombination rate.

The equation governing the exciton dissociation is given by:

$$R_D np = \frac{3 r_L}{4\pi \texttt{A.SINGLET}} exp\left(-\frac{\texttt{S} \cdot \texttt{BINDING}}{kT}\right) \frac{J_1(2\sqrt{-2b})}{\sqrt{-2b}}$$

Here r_L is the Langevin recombination rate constant. A.SINGLET and S.BINDING are user specified parameters representing the electron hole pair distance and the singlet exciton binding energy, J_1 is the first order Bessel function, S is the singlet concentration and the b parameter is given by:

$$b = \frac{q^3 |E|}{8\pi \varepsilon_r \varepsilon_0 k^2 T^2}$$

where E is the local electric field, ε_r is the relative permativity and T the temperature.

We also added a parameter, QE.EXCITON that describes the fraction of absorbed photons that generate singlets (as opposed to electron hole pairs). Generally this parameter should be assigned to one. We should note that all of the optical absorption models available in our Luminous simulator are also available in Organic Solar. These include geometric ray tracing, transfer matrix, beam propagation and finite difference time domain methods.

To calibrate this model we attempted to reproduce the experimental results presented in the Korster paper. These measurements were performed on a 120 nm thick OC_1C_{10}-PPV/PCBM (20:80 wt %) BHJ solar cell. The authors suggested the parameter values shown in Table 1.

The singlet binding energy, S.BINDING, was not specified but a value less than 0.4 eV was implied. We chose as a baseline to use 0.35 eV.

Parameter	Symbol	Value	Units
Band Gap	Eg	1.34	eV
Electron mobility	μn	2.5×10^{-3}	cm²/Vs
Hole mobility	μp	3.0×10^{-4}	cm²/Vs
Eff. density of states	Nc/Nv	2.5×10^{19}	cm⁻³
Relative permittivity	Ɛr	3.4	
Pair distance	A.SINGLET	1.3	nm
Decay Rate	KNRS.EXCITON	1.5×10^{6}	s⁻¹

Table 1: Suggested Parameter Values

As for photogeneration, the authors suggested a constant photogeneration rate throughout the device of 2.7×10^{21} cm⁻³s⁻¹. Our own calculations indicate that for complete light collection of AM1.5 solar spectrum a value of 3.6×10^{22} cm⁻³s⁻¹ would be appropriate. The latter value ignores front reflections or light passing through the device.

Based on the suggested parameter values we ran the simulation. Figure 1 shows the comparison of our simulation with the presented experimental results. Although the short circuit current is a good match, the remainder of the curve varies quite a bit from the experiment. Due to our lack of knowledge of various parameters and models such as the Langevin recombination model in the Korster paper, we decided to use the DeckBuild Optimizer to tune the result.

The DeckBuild Optimizer is a multi-target, multi-parameter optimization tool that uses the modified Levenberg-Marquart algorithm to build a response surface of results versus input parameters as the iterations progress. The interface is conveniently embedded inside of DeckBuild and presents the user with easy to use worksheet based
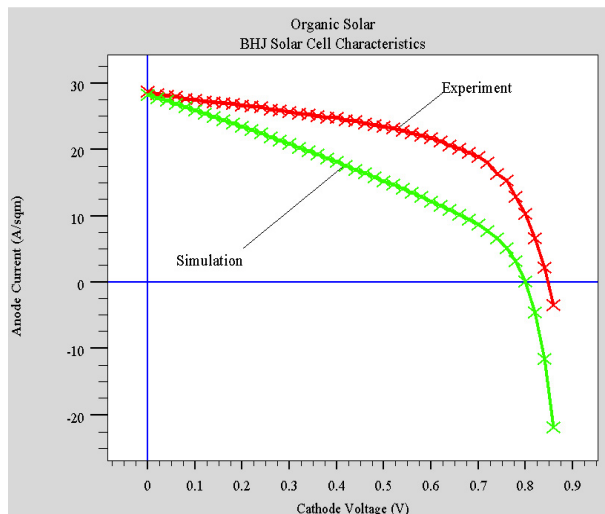

Figure 1. Organic Solar Cell comparison of experimental versus un-optimized simulated current-voltage characteristics.

Parameter name	Response type	Optimized value	Initial value	Minimum value	Maximum value
material knrs.exciton	linear	1.82694e+06	1.5e6	750000	2.25e+06
material a.singlet	linear	1.32167	1.3	0.65	1.95
material s.binding	linear	0.28464	0.4	0.2	0.6
solve b1	linear	0.587647	1.0	0.5	1.5

Figure 2. Organic Solar Cell optimizer parameter worksheet.

GUI. We felt that this application was well suited to such an approach since the simulations were one dimensional and thus fast and there were few input parameters.

The input parameter worksheet is shown in Figure 2.

Here we can see that we chose the decay rate (KNRS. EXCITON), the pair distance (A.SINGLET), the binding energy (S.BINDING) and a scale factor on the photogeneration rate (B1) as the variable parameters. The target was chosen as the digitized experimental data as shown in Figure 1.

Then with a single mouse click the optimizer performs a series of iterations of running the simulation automatically adjusting the input parameters each simulation until convergence to the target is met. The results of each iteration are shown on the Optimizer Results worksheet shown in Figure 3.

Here we see that convergence was obtained in only 14 iterations. A comparison of the experimental results with the optimized and unoptimized results is shown in Figure 4.

We see that a good match has been obtained, not just in the short circuit current, but also the open circuit voltage and the entire curve.

If we return to the results worksheet in Figure 3, we can examine how the input parameters were changed to match the experimental results. In comparison with the original parameters we can see that the decay rate and electron-hole spacing are reasonably close to the original values.

Iteration	material knrs.exciton	material a.singlet	material s.binding	solve b1	IV	Sensitivity
1	1.5e+06	1.3	0.35	1	err=46%	---
2	1.54743e+06	1.3	0.35	1	err=47%	69%
3	1.5e+06	1.34111	0.35	1	err=50%	2.7e+02%
4	1.5e+06	1.3	0.361068	1	err=64%	1.2e+03%
5	1.5e+06	1.3	0.35	1.03162	err=44%	-1.4e+02%
6	1.64488e+06	1.32324	0.321206	0.762386	err=25%	---
7	1.78231e+06	1.34459	0.296588	0.5	err=31%	---
8	1.76051e+06	1.34494	0.300619	0.566989	err=25%	---
9	1.76525e+06	1.34494	0.300619	0.566989	err=25%	---
10	1.76051e+06	1.34905	0.300619	0.566989	err=26%	---
11	1.76051e+06	1.34494	0.301726	0.566989	err=27%	---
12	1.76051e+06	1.34494	0.300619	0.570152	err=25%	---
13	1.70478e+06	1.29676	0.287825	0.58442	err=2%	---
14	1.82694e+06	1.32167	0.28464	0.587647	err=1.7%	---

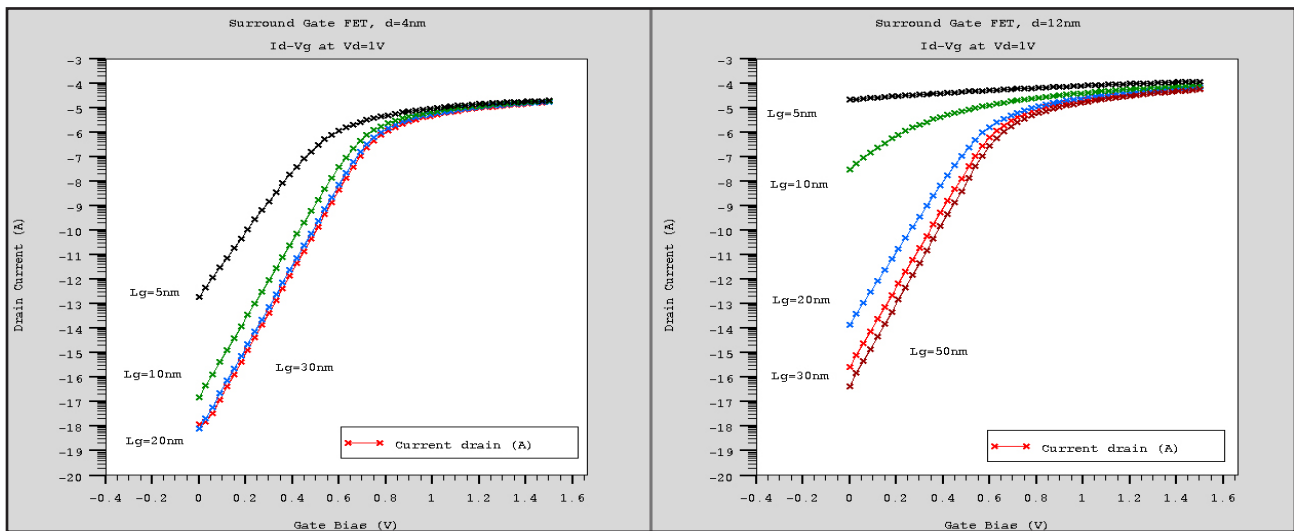Figure 3. Organic Solar Cell optimizer results worksheet.

Figure 9. Gate length scaling of surround gate FETs with diameter of 4nm (left) and 12nm (right).

Introduction

The Drift-Diffusion Mode-Space model (DDMS) is a semi-classical approach to transport in devices with strong transverse confinement. The solution for carrier density and current is decoupled into 1D, 2D or cylindrical Schrödinger equation in transverse direction and 1D classical drift-diffusion equation to account for carrier transport in each subband. Thus, the model rigorously captures quantum effects in transverse direction and yet inherits all familiar ATLAS models for mobility, recombination, impact ionization, and band-to band tunneling.

Simulation

Usage of DDMS is quite analogous to that of Schrödinger or mode-space NEGF models. The DDMS models is activated by an option DD_MS along with SCHRO (for electrons) and/or P.SCHRO (for holes) on the MODELS

statement. Variable CARR on the METHOD statement should be set to zero, since multidimensional drift-diffusion solvers are not used. Due to a variation of electron density and potential in transverse direction, Dirichlet boundary conditions in contacts are not the best option. Instead, a quasi Fermi level is fixed, while electrostatic potential is subjected to von Neumann (zero electric field) boundary conditions, which are set by specifying REFLECT on the CONTACT statement.

Schrödinger equation is solved in each transverse slice to find electron and/or hole eigen energies and wave functions. The minimum required number of eigen states is determined automatically, but may also be set by parameter EIGEN on the MODELS statement. The DDMS model is compatible with all ATLAS Schrödinger solvers: 1D and cylindrical in Atlas2D and 2D in Atlas3D. Position dependent eigen energies play a role of conduction (valence) band
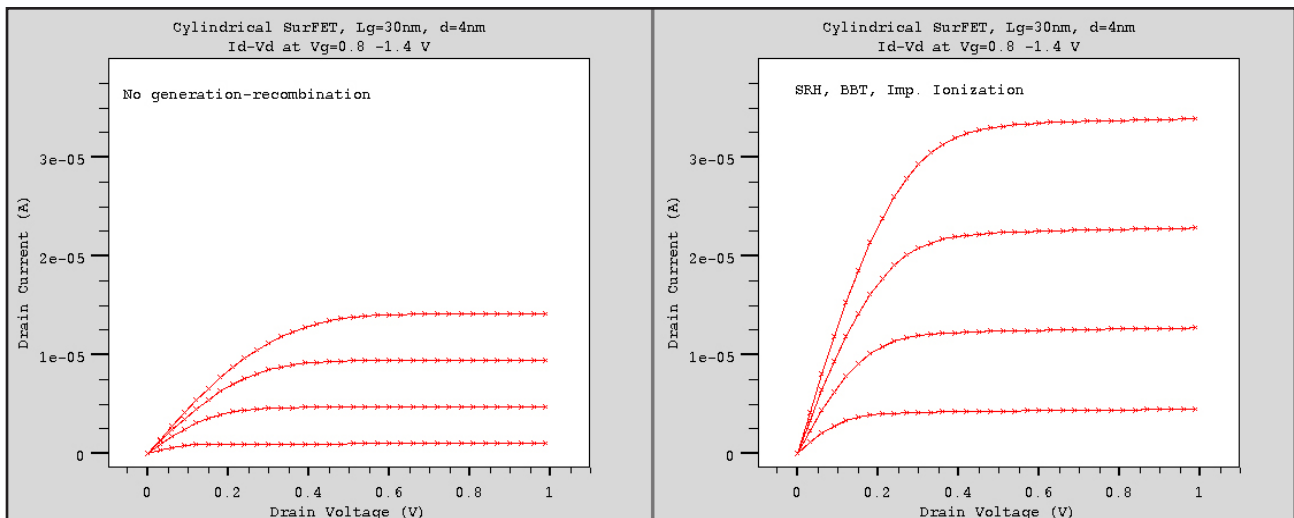

Figure 10. Id-Vd characteristics of surround gate FETs (Lg=30nm D=4nm) in the absence (left) and in the presence (right) of generation-recombination.
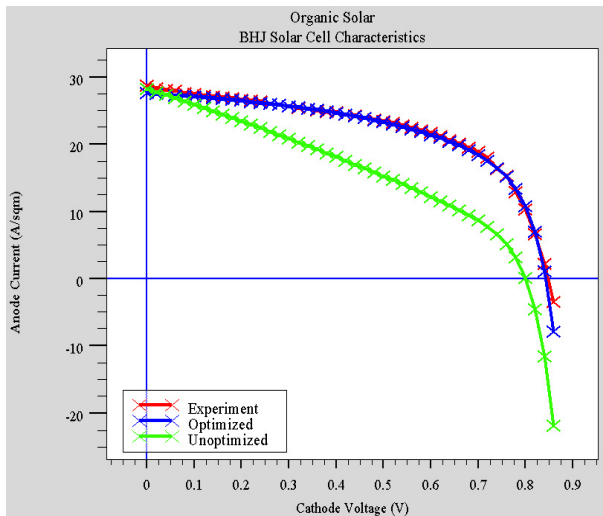
Figure 4. Organic Solar Cell comparison of experimental versus optimized simulated current-voltage characteristics.

The binding energy has changed somewhat but we can take comfort in the fact that value used by Korster et al was not given. Finally we see that the photogeneration rate was reduced to roughly 58% of the suggested value. With respect to experiment this seems reasonable since the assumed constant generation rate was probably not measured. In all we are quite satisfied with the tuning experiment and feel confident that such an approach can be applied to other devices/materials.

Before concluding we would like to remark that we used the Optimizer simply as a tuning device.

For more complicated situations such as larger simulations with many unknowns we acknowledge that the Optimizer may not be the best approach. We also point out that the number of inputs can usually be reduced. For example referring back to equation 2 we note that A.SINGLET and S.BINDING could have been replaced by a single parameter in the optimization.

Conclusion

In conclusion, we have demonstrated the newest TCAD device simulation tool at Silvaco. We feel confident that Organic Solar can be of use in the accurate prediction of preformance of organic solar cells. We have also demonstrated in a practical example the use of the DeckBuild Optimizer.

References

(1) Korster, L.J.A, Smits, E.C.P., Mihailetchi, V.D., and Blom, P.W.M. "Device model for the operation of polymer/fullerene bulk heterojunction solar cell", Physical Review B, Vol. 72, (2005) pp. 085205-1, 085205-9.