An introduction with space charge limited conduction in organic light emitting diodes

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Abstract: In all previous research about organic light emitting diodes, have studied the mobile ion movement in an externally applied electric field. In those researches also used a simple model to calculate the induced voltage shifts. The simple model assumes a constant electric field and only considers a direct contribution from the redistribution of mobile ions on the operating voltage. In a real OLED, the injected electrons and holes are also charged particle. When the mobile ions are introduced, the distribution of electrons and holes as well as the potential profiles can be perturbed in a more complicated way than what has been discussed on those researches which is observed in our experiments. As a matter of fact, the two transport problems, namely, that of the mobile ions and that of the current carriers (electron and hole), are coupled together and needs to be solved self-consistently. Because the time scaled of the two problems are orders of magnitude different, we can treat the case in a quasi-static way, namely, by considering the mobile ions to be stationary when we solve the carrier transport problems. Before taking that task, we first consider the current carrier (electron and hole) transport problem in this paper. We will then propose numerical solution based on finite difference method and discuss about it.

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1. Introduction

The conductivity of the typical organic materials (e.g. Alq3) recently being used for OLED applications (Iwama et al, 2006) lies between that of a good insulator and that of a good semiconductor (e.g., Si or GaAs). So one can either call them semiconductors or semi-insulators. The reasons why the organic materials are less conductive than the inorganic semiconductors are due to the lack of conducting carriers and due to the low carrier nobilities (~10-4 cm2/V.s or less). The amorphous nature of the organic materials results in band tail states (or deep traps) so that most of the injected carriers often hop through these slowly. Also, because the lack of an efficient scheme of doping the organic material to produce conducting carriers, the carriers are basically injected from the electrodes, resulting in space charge clods near the electrodes and the space charge limited conduction (SCLC) theory has been governed as main tunneling mechanism (Nesporek et al, 2008).

Analytical and numerical models have been established for carious situations. Here we outline the main equations and present analytical solutions to a simple case and numerical solutions to more general cases. In this included our aim is to develop a working model describing carrier transport effects so that we can study the perturbation by mobile ions.

2. Formalism

The equations describing the space charge limited conduction problem are the coupled one-dimensional Poisson and current equations:

$$\frac{d^2u(x)}{dx^2} = -\frac{q}{\varepsilon}[p(x)-n(x)], \quad (1)$$

$$\frac{dJ_n(x)}{dx} = -\frac{dJ_p(x)}{dx} = qK_b[n(x)p(x)-n_i^2] \quad (2)$$

$$J_n(x) = -q\mu_n(x)n(x)\frac{dU(x)}{dx} + qDn(x)\frac{dn(x)}{dx}, \quad (3)$$

$$J_p(x) = -q\mu_p(x)p(x)\frac{dU(x)}{dx} - qD_p(x)\frac{dp(x)}{dx}. \quad (4)$$

Where U is the electrostatic potential; n, p, and n_i are the free electron, free hole and intrinsic carrier concentrations, respectively; J, μ, and D are the current density, mobility, and diffusion constant, respectively, with subscripts labeling the corresponding species (n for electrons and p for holes); K_b is the recombination coefficient; q is the electronic charge; ε is equal to $\varepsilon_0 \varepsilon_r$ with ε_0 being the permittivity of vacuum and ε_r the relative dielectric constant. We introduce two quasi-Fermi (Brennan, 2005) levels ($F_n and F_p$) and express the carrier concentrations as follows:

$$n = n_i e^{(F_n+qU) / KT}, \quad (5)$$

$$p = n_i e^{(-F_p-qU) / KT}, \quad (6)$$

The boundary conditions used in this work are assumed to be

$$F_0(0) = F_p(0) and F_n(L) = F_p(L), \quad (7)$$

$$P(0) = P_0 and n(L) = n_0 \quad (8)$$

Where L is the organic layer thickness. The p_0 and n_0 are adjustable parameters determining the amount of carrier injection at the electrodes.

3. Simple Analytical Solutions Neglecting Diffusion Term

In the case where only one kind of carrier is considered, simple analytical solutions can be obtained readily by ignoring the diffusion term. The derived current-voltage dependence has power-law dependence:

$$J = \frac{9}{8} \mu \varepsilon \frac{V_A^2}{L^3}. \quad (9)$$

Which is the Child's law (Rieser, 2008). Equations (1) – (8) do not generally have analytical solutions when both carriers are included. However, in some special cases, for example, analytical solutions have been obtained and used to analyze the special characteristics of the space charge limited conduction process. In that treatment, the diffusion term is generally neglected and ohmic boundary conditions are used. Below, we derived a set of analytical solutions to the double-carrier problem by assuming ohmic boundary conditions, neglecting diffusion terms, and by assuming an infinitely large recombination coefficient (k_b). The last assumption above basically means the recombination zone is infinitely narrow, and we can partition the OLED into a complete p-type region on the anode side and a complete n-type region on the cathode side.

The double-carrier problem can be simply reduced to two single-carrier problems and then put together by imposing the current continuity condition. The infinitely large K_b assumption may not be realistic; nevertheless, the obtained analytical solutions do reveal some interesting physics and can also be used to compare the numerical solutions we will present afterwards. The analytical solutions are:

$$n(x) = \begin{cases} 0 & for\ 0 \prec x \prec L/2 \\ (\frac{9\varepsilon^2 V_A{}^2}{8L^3 q^2 x})^{1/2} & for\ L/2 \prec x \prec L \end{cases} \quad (10)$$

$$p(x) = \begin{cases} (\frac{9\varepsilon^2 V_A{}^2}{8L^3 q^2 x})^{1/2} & for\ 0 \prec x \prec L/2 \\ 0 & for\ L/2 \prec x \prec L \end{cases} \quad (11)$$

$$E(x) = \begin{cases} (\frac{9V_A{}^2}{2L^3} x)^{1/2} & for\ 0 \prec x \prec L/2 \\ \left[\frac{9V_A{}^2}{2L^3}(L-x)\right]^{\frac{1}{2}} & for\ L/2 \prec x \prec L \end{cases} \quad (12)$$

$$J_p = \begin{cases} \frac{9\mu\varepsilon V_A^2}{4L^3} & for\ 0 \prec x \prec L/2 \\ 0 & for\ L/2 \prec x \prec L \end{cases} \quad (13)$$

$$J_n = \begin{cases} 0 & for\ 0 \prec x \prec L/2 \\ \frac{9\mu\varepsilon V_A^2}{4L^3} & for\ L/2 \prec x \prec L \end{cases} \quad (14)$$

Where V_A is applied voltage, and we have assumed $\mu_n = \mu_p$ for the purpose of simplicity. The results are plotted in Fig. 1, where electric field is highly non-uniform, and maximum electrical field is located at middle of device. The carrier densities decay rapidly near electrodes. Since no diffusion term is included, the carrier concentrations at both anode and cathode become infinity in order to satisfy current continuity.

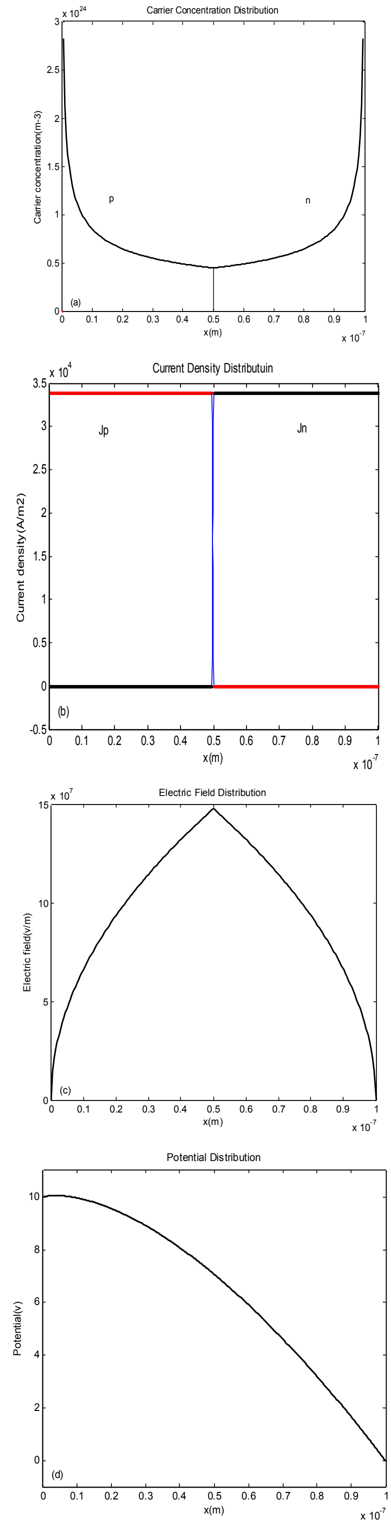


Fig. 1. Double carrier injection space charge limited conduction model neglecting diffusion. The parameters used for this simulation are: $L = 100nm, \varepsilon_r = 3.4, V_A = 10v, \mu_n = \mu_p = 5\times10^{-9}\, m^2/vs$ and ohmic contact boundary condition.

4. Numerical Solutions

We employed finite difference method to solve the equations (Mitchel et al, 1980). The Eq. (1) is discretized to an associated difference equation, which is constructed using a centered difference quotient to replace the derivative. The difference equations associated with Eqs. (2), (3) and (4) are obtained in the similar manner. The discretization gives rise to a nonlinear system of equations. To achieve a better convergence, Gummel's method (Chen, 2003) is used. In this approach $J_n, J_p, \mu_n, \mu_n,$ and E are treated as constants between mesh points ($i, i+1$); then, equations (3) and (4) can be solved analytically within this mesh. And the results are expressed as:

$$J_n(x) = q\mu_n(x_i)E(x_i)\left(\frac{n(x_i)e^{\frac{-hqE(x_i)}{KT}} - n(x_{i+1})}{e^{\frac{-hqE(x_i)}{KT}} - 1}\right) \quad (15)$$

$$J_p(x_i) = q\mu_p(x_i)E(x_i)\left\{\frac{P(x_i)e^{\frac{hqE(x_i)}{KT}} - p(x_{i+1})}{e^{\frac{hqE(x_i)}{KT}} - 1}\right. \quad (16)$$

Where $h = x_{i+1} - x_i$ and E(x_i) is the electric field.

Since the system of equations is nonlinear there is no deterministic path to the solution, and iteration is necessary. In our work the Poisson equation is solved with the quasi-Fermi potentials held fixed, then the continuity equations are solved using the new values of potential. The cycle begins again with the new quasi-Fermi levels just computed. The whole iterative process stops when both potential and Fermi levels meet desired precision. The detailed procedures are shown in Fig. 2.

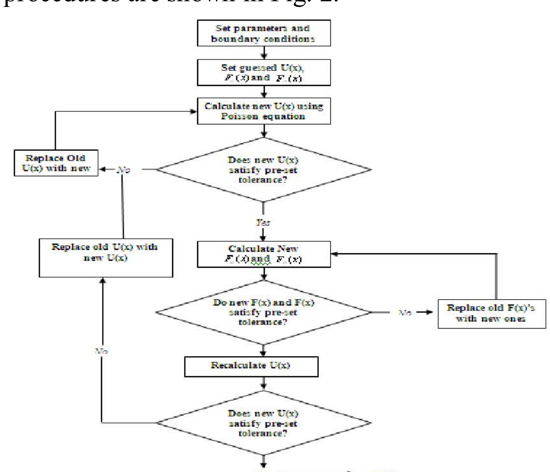


Fig. 2. Flow chart of simulation

Evaluating the solution, several cases are simulated in this work. In Fig. 3 we consider a 100 nm long, ohmic contact.

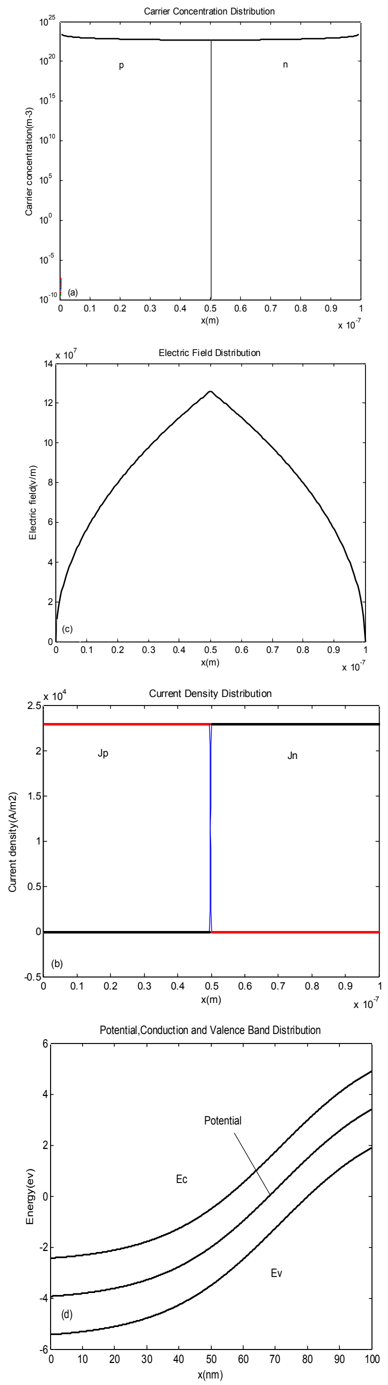


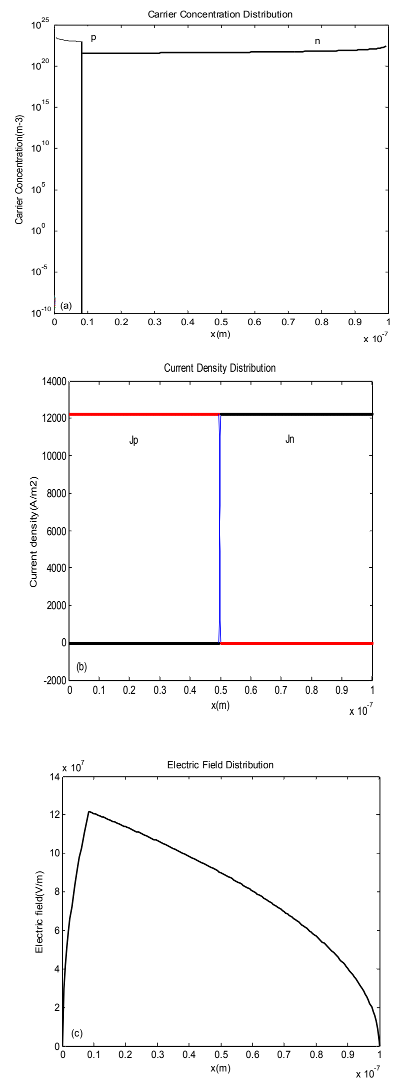
Fig. 3. Double carrier injection SCL numerical solutions with ohmic contact boundary conditions. The parameters used for this simulation are:

$L = 100nm, \varepsilon_r = 3.4, V_A = 10v, \mu_n = \mu_p = 5\times10^{-9}\, m^2/_{vs}, E_G = 2.8ev, K_b = 1\times10^{-10}\, m^3/_{s},$
$p_0 = n_0 = 3.1\times10^{24} m^{-3}, n_i = 10^6 m^{-3}, T = 300k.$

To obtain an ohmic contact boundary condition, the p_0 and n_0 in equation (8) are adjusted gently and carefully until zero electric fields at both cathode and anode are reached. Since the p_0 and n_0 represent the carrier concentrations at electrodes they are large numbers in non-interfacial-resistance condition. By comparing Fig. 3 with Fig. 1, we find that the numerical model converges to a correct solution.

Since diffusion term is included in numerical model, the p_0 and n_0 are finite.

Fig. 4 shows the case where the hole mobility is less than electron mobility, and all other parameters are held same as in Fig. 3.



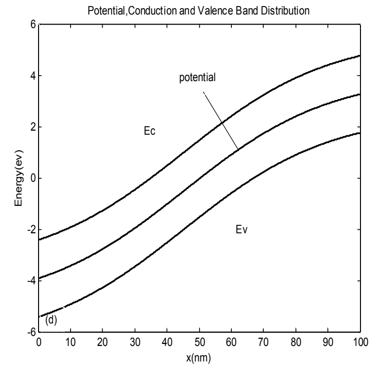
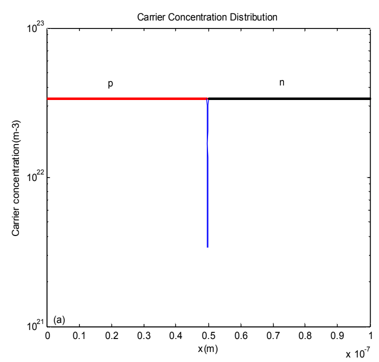
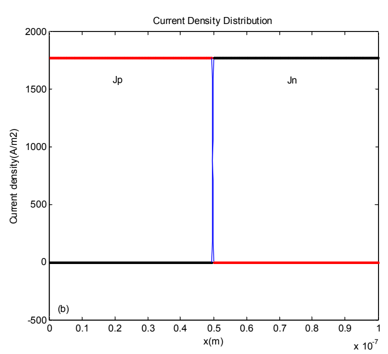


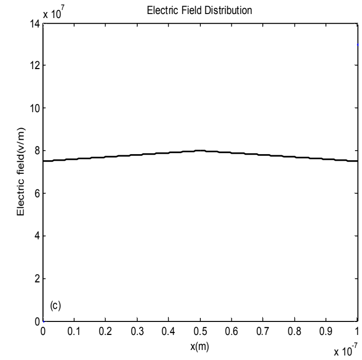
Fig. 4. Double carrier injection SCL numerical solutions with asymmetrical nobilities. The parameters used for this simulation are:

$L=100nm, \varepsilon_r=3.4, V_A=10v, \mu_n=5\times10^{-9}\,m^2/_{VS}, \mu_p=5\times10^{-10}\,m^2/_{VS}, E_G=2.8ev,$
$K_b=1\times10^{-10}\,m^3/_S, p_0=n_0=3.1\times10^{24}\,m^{-3}, n_i=10^6\,m^{-3}, T=300k.$

Due to the unbalanced motilities, the recombination zone is not at middle, but shifts towards anode. Correspondingly, the peak of the electric field also moves towards anode. The electric field at both electrodes is not zero even though the p_0 and n_0 are kept same as in Fig. 3. This indicates strong coupling effect within the system. In Fig. 5 an example of SCL subject to blocking boundary conditions is presented. Under blocking boundary conditions, the carrier densities and the variation of carrier concentration over length become smaller.







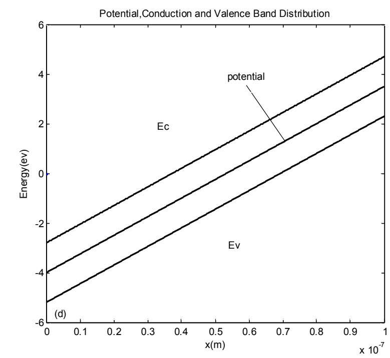
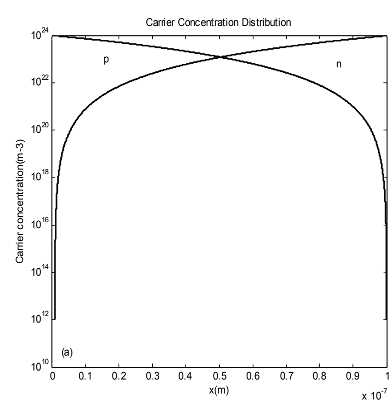


Fig. 5. Double carrier injection SCL numerical solutions with blocking boundary conditions. The parameters used for this simulation are:

$L=100nm, \varepsilon_r=3.4, V_A=10v, \mu_n=\mu_p=5\times10^{-9}\,m^2/_{VS}, E_G=2.8ev, K_b=1\times10^{-10}\,m^3/_S,$
$p_0=n_0=3.1\times10^{22}\,m^{-3}, n_i=10^6\,m^{-3}, T=300k.$

The electric filed distribution tends to be uniform. Lowering the variation in carrier densities and electric field indicate a less space charge effects. Finally, we simulated a particular case with a small recombination coefficient. The results are shown in Fig. 6. Two particular features are associated with small recombination coefficient. (i) The recombination zone extends; (ii) The current densities for both hole and electron can be very large.



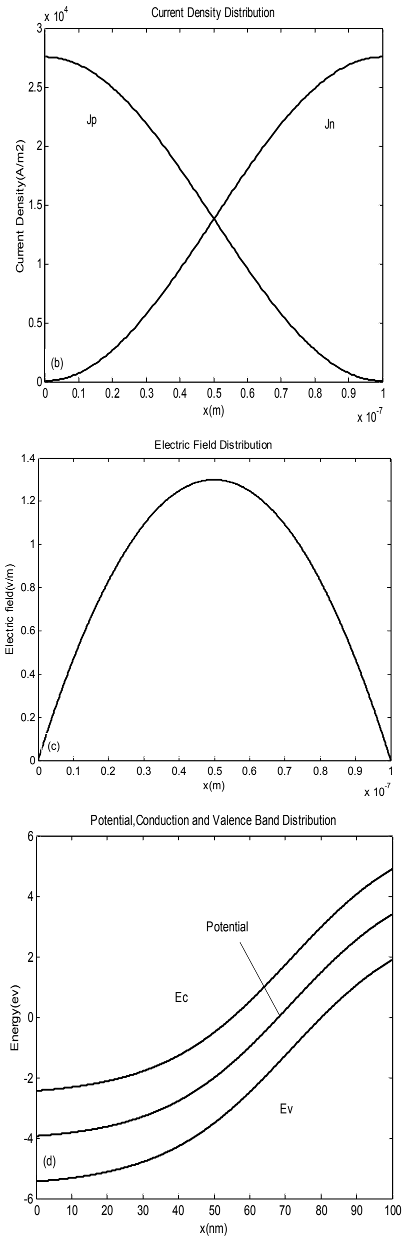


Fig. 6. Double carrier injection SCL numerical solutions with small recombination coefficient. The parameters used for this simulation are:
$L=100nm, \varepsilon_r=3.4, V_A=10v, \mu_n=\mu_p=5\times10^{-9}\, m^2/vs, E_G=2.8ev, K_b=1\times10^{-16}\, m^3/s,$
$p_0=n_0=3.1\times10^{24}\, m^{-3}, n_i=10^6\, m^{-3}, T=300k.$

5. Discussion of Solutions

According to their conduction properties, the OLED materials can probably be classified as either semiconductors or insulators. Their typical band gap is about 3 ev, and the device is usually undoped in terms of conduction type. Thus, the current carriers have to be injected from the electrodes. According to the properties of contacts, the conduction could either be space charge limited or contact limited. For a large energy barrier contact organic bulk electric resistance becomes less important, and the total current density is determined by thermionic emission or tunneling from electrodes. When the energy barrier between contact and organic material is small, the conduction is space charge limited, and current-voltage relationship obeys the classic Child's square law: $J \sim V^2$ as shown in Eq. (9). This relationship deviates from a linear form because the carrier distribution is not a constant in the solid; but rather, it decays rapidly into the solid from the injecting electrode.

•Diffusion Effect

Neglecting diffusion term does not change the physics over most of region: but it does create singularity under ohmic contact assumption. As mentioned above, the p_0 and n_0 approach infinity at x=0 and x=L due to current continuity requirement. However, when diffusion term is included, the diffusion current itself warranty the current continuity at boundaries without requiring infinitely high values of p0 and n0 Nevertheless, the approximate theoretical model without diffusion effect provides a simple tool to understand the SCL physics and a reference to test the validity of numerical solutions. Since the carrier distribution is highly nonuniform under ohmic contact boundary conditions, neglecting diffusion is not justified; however our simulation result shows that for a highly blocking contact diffusion becomes less important (Fig.5). This observation is in agreement with Davids et.'s analysis (Davids et al, 1997).

In a more general situation diffusion plays an important role near contact regions where the diffusion effects push carriers away from the contact and into the regions of lower concentration in the bulk. Including diffusion effects sometimes leads to a negative electric field near the electrode (Fig. 4d). It appears that diffusion is so strong near electrodes that electric field has to be negative to achieve current continuity. The negative electric field near electrode can be interpreted as a very strong space charge effect, which prohibits drift current within near electrode region. Theoretically. If no any electrical resistance exists between contact electrode and organic material, carriers ($\sim 10^{22}\, cm^{-3}$) in metal will lead to a strong diffusion current into organic layer. In reality, existence of negative electric field near electrodes is questionable.

•Current Density

In our model current continuity is enforced, therefore the total current density is a constant in each studied case. In general hole current is dominant in anode region, and electron current in this region has reduced to a undetectable level provided that the recombination coefficient is large enough; conversely, in cathode region electron current dominates. Providing a small recombination constant it is easy to understand that the hole and electron currents co-exist over the whole region of device. The space charge effect becomes weak due to the cancellation of positive and negative charges. All the current densities in this work are relatively large ($0.184 \sim 3.38 A/cm^2$) compared to typical experiment value of about $0.1 A/cm^2$ at 10 volt bias. The reason for the large currents id due to choice of parameters and ignorance of some physical components such as charge traps.

The current density achieves its maximum value if the contact is ohmic, since ohmic contact and organic materials, so contact can provide sufficient carriers. At blocking contact condition the current density decreases (Fig. 5a), since at this condition the OLED is operating at near contact limited regime. So as we know that OLED could operate in injection limited regime of space charge limited regime, most likely in the transition regime between injection limited and space charge limited.

Charge injection into the organic material can occur by thermionic emission and by tunneling. It is generally believed that for Schottky energy barriers less than about 0.3~0.4 eV, for typical organic LED device parameters, the conduction is space charge limited, .However, for large energy barriers the current flow is injection limited, and in this regime, the net injected charge density is relatively small. For instance, the anode injection current can be written as:

$$J_p(0) = J_{th} - J_{ir} + J_{tu} \quad (17)$$

Where J_{th} is the thermo ionic emission current density , J_{ir} is the back flowing current density and J_{tu} is the tunneling current density. The thermo ionic emission current density is calculated using an energy barrier that depends on the electric field at the interface because of image force effect.

$$J_{ih} = AT^2 e^{-\Phi 1KT} e^{\frac{q}{KT}\sqrt{\frac{qE(0)}{\varepsilon}}} \quad (18)$$

Where A is Richardson's constant (Zeghbroeck, 2008), T is the temperature and Φ is the Schottky energy barrier at zero field. The back flow is proportional to the hole density at the interface

$$J_{ir} = VP_0 \quad (19)$$

where the kinetic coefficient is determined by detailed balance between the thermo ionic emission and back flow. The tunneling current, which plays an role only in large bias case, is calculated using the WKB approximation for tunneling through a potential.

Because the mobility represents the rate of carrier transport, thus it is understand at lower mobility the current density will reduce as shown in Fig. 4a.

It is worth noting that all numerical simulated potential differences of two electrodes (Fig. 3.c ~ Fig. 6.c) are about 8.0 volt instead of applied voltage of 10 volt. The simple explanation is that built-in voltage has been included in numerical model. In our simulation model one relation was used:

$$F_n(L) - F(0) = qV_{A.} \quad (20)$$

This relation more accurately reflects the reality if any built – in voltage involved. In OLED since the work – function difference between metal contact and organic material, there is a built – in voltage across the interface. Another part of built – in voltage comes from work function difference between two metal contacts materials.

•Electric Field

For the ohmic contact there is no voltage drop across the interface. Thus the electric fields at boundaries are zero. Over the entire range of device the electric field is highly non-uniform. As the contacts become blocking, electric field is needed for carriers to surmount the surface barriers. Because of constant applied voltage, which is equal to the area beneath the electric field curve. The electric field distribution tends to be nearly uniform. For an extreme case where the contact is total blocking the OLED reduces to a leaking capacitor – like device, in which the charge densities are trivial, and the electric field distribution is completely uniform. The electric field distribution plays a very important role in the movement of mobile ions.

Figures 4.d and 6.d show that the parameters such as mobility and recombination coefficient also affect the electric field distribution. The carrier transport parameters determine the charge distribution inside the system, in turn; the electric field distribution has to accommodate the change of charge distribution. The rise of electric field at anode shown in Fig.4 implies the depletion of injecting source, in other words, the contact was not able to supply enough carriers to the bulk.

•Recombination Coefficient

For sufficiently large recombination coefficient the recombination takes place rapidly and the recombination zone is confined within a relatively thin region (-3 nm); for a small recombination constant the size of recombination zone could extend over the entire length of device (Fig. 6), and also the current density increases. The increase of current density is attributed to the carrier densities being held high over entire device for small K_b.

The location of recombination zone is dependent on the difference of hole mobility and electron mobility. For identical motilities of holes and electrons, it is understandable that the recombination zone is located at the middle of length due to symmetry of all quantities. As a result of small hole mobility the recombination zone shifts towards the anode since the electrons travel further than the holes do. In this case, the hole concentration is apparently higher than the electron concentration; this phenomenon is originated from the requirement of charge neutrality. The location of recombination is of special importance zone where the electron-hole pair forms, and the exciton diffuses into layer to emit light. If the dye layer is far from recombination zone, the efficiency of emitting will reduce.

•Boundary Conditions

Mathematically, a differential boundary-value problem requires two boundary conditions for a certain solution. The Eqs. (2) – (4) can be collapsed into two boundary-value equations. Therefore, six boundary conditions for the system are sufficient. In our work it was found that the boundary condition (7), which implies an equilibrium state for carriers, was a good assumption. The simulation results suggest that the carriers achieve quickly an equilibrium state over most the region for a typical recombination coefficient used in this simulation work. Even for a relatively small recombination coefficient, the boundary condition of Eq. (7) still leads to reasonable physical results. However the boundary condition Eq. (8) sometimes leads to an arguable physical picture if using without care. It is generally believed that n_0 and p_0 are of high value between $10^{13} \sim 10^{20} cm^{-3}$ and a value as high as is suggested for ohmic contact. It is important to note that the n_0 and p_0 represent the carrier densities at both contact interfaces. These values might not always be assumed arbitrarily. The negative electric field has been suggested due to the carrier diffusion from metal contact. In our opinion, accommodation of carriers in organic material might not be unlimited, and it should depend on the physical and electrical properties of materials. In our simulation work, it was found that the n_0 and p_0 need to be adjusted to achieve a perfect ohmic contact for a different combination of mobility and recombination constant; this parameter combination might imply a different electrical characteristic of the material.

The negative electric field can not be a real existence but results from a too high setting for carrier concentration at boundaries. Further analysis indicates that arbitrarily high carrier density leads to an unreasonable large diffusion current, which needs an opposite drift current (negative field) to meet the current conservation mathematically.

6. Conclusion

By the method proposed in this paper, ion transport equation in organic light emitting diode can be studied.Firstly; the solution of PDE equations which govern on transport equation, obtained neglecting diffusion term explicitly and then finite difference method was used to solve a PDE problem. Changing the equation's parameters led to effectiveness determination of these parameters to ion transportation.

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References

1. Y. Iwama, T. Itoh, T. Mori, T. Mizutani, Thin Solid Films. 499, 364 (2006).
2. S. Nesporek, O. Zmescal, J. Sworakowski, Thin Solid Films. 516, 8949 (2008).
3. K. F. Brennan, Introduction to semiconductor devices: for computing and telecommunications, (Cambridge University Press, 2005).
4. M. Rieser, Theory and Design of Charged Particle Beams (Wiley-VCH, 2008).
5. A. R. Mitchel, D. F. Griffiths, the Finite Difference Method in Partial Differential Equations (John-Wiley, 1980).
6. R. C. Chen, J. L. Liu, Journal of Computational and Applied Mathematics. 159, 341 (2003).
7. P. S. Davids, I. H. Campbell, D. L. Smith, J.Appl.Phys. 82, 6319 (1997).
8. B. V. V. Zeghbroeck, Principles of Semiconductor Devices and Heterojunctions (Prentice Hall, 2008).

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