Doping Dependent Conductivity in Organic Semiconductors

Ling Li, Gregor Meller, and Hans Kosina
Institute for Microelectronics, TU Wien, Gußhausstraße 27–29/E360, 1040 Wien, Austria
e-mail: ling.li@iue.tuwien.ac.at

***Abstract*— Charge transport in doped organic semiconductors is investigated, and an analytical conductivity model is formulated. This model can explain the temperature dependence of conductivity and the change in conductivity of an organic semiconductor upon doping. The results agree well with recent experimental data.**

I. INTRODUCTION

After the discovery of electroluminescence in the conjugated polymer PPV [1], [9] and its derivatives, much effort has been devoted to the study of the (opto)electronic and electrical transport properties. Understanding the carrier transport properties in these organic materials is of crucial importance to design and synthesize better materials and to improve device performances. However, a proper theoretical description of charge transport in organic semiconductors is still a challenge. In organic semiconductors, intramolecular interactions are mainly covalent, whereas intermolecular interactions are due to much weaker van der Waals and London forces. As a result, the transport bands in organic crystals are much narrower than those of their inorganic counterparts, and the band structure is easily disrupted by disorder in such systems. This disorder causes the formation of localized states in the energy gap. In order to enable a current through the device, charge carriers trapped at the localized states need to escape from these sites. Such a conduction process is entirely determined by the tunneling transitions of carriers between the localized states, provided that the electronic wave functions of the localized states have sufficient overlap. This theory was originally given by Conwell [2] and Mott [6]. A more systematic theory called variable range hopping (VRH) was introduced by Mott in 1968 [8]. The transport properties of organic semiconductors can be well described by VRH theory [12], [14], [15].

Despite over 25 years development, some rather ubiquitous features of charge transport in organic semiconductors are still not well understood. One primary example is the relation between conductivity and doping [11], [16]. Although it is known for a long time that the conductivity of organic layers can be enhanced remarkably by coevaporation with strong organic π-electron donors or acceptors [13], organic devices are usually prepared in undoped form. However, the electrical properties of undoped layers are governed by uncontrolled impurities or by gases such as oxygen [10]. At the same time, the breakthrough of microelectronics technology make it possible to improve device properties by controlled doping [3], [5].

The doping process of organic semiconductors can largely be described by a standard model used for a crystalline anorganic semiconductors [4]. However, a proper doping model is still a challenge for organic semiconductors, for example, it is not known whether the dopants are homogeneously distributed in the material. In particular, the reason for the strong superlinear increase of the conductivity with doping observed in some experiments is unclear [22].

In this work, we present an analytical model of hopping transport in doped disordered organic semiconductors based on VRH theory and percolation theory. This model shows the superliner increase of conductivity with doping observed in several experimental data sets.

II. MODEL

For a disordered organic semiconductors system, we assume that localized states are randomly distributed in both energy and coordinate space, and that they form a discrete array of sites. Conduction proceeds via hopping between these sites. In the case of low electric field, the conductivity between site i and site j can be calculated as [17]

$$\sigma_{ij} \approx \gamma \exp - (s_{ij}) . \tag{1}$$

with

$$s_{ij} = 2\alpha R_{ij} + \frac{\mid \epsilon_i - \epsilon_F \mid + \mid \epsilon_j - \epsilon_F \mid + \mid \epsilon_i - \epsilon_j \mid}{2k_B T}$$

where ϵ_i and ϵ_j are the energies at the sites i and j, respectively, ϵ_F is the Fermi-energy, R_{ij} is the distance between sites i and j, and α^{-1} is the Bohr radius of the localized wave function. The first part of s_{ij} is a tunneling term and the second one is thermal activation term (Boltzman term).

For organic semiconductors, the manifolds of both lowest unoccupied molecular orbitals (LUMO) and highest occupied molecular orbitals (HOMO) are characterized by random positional and energetic disorder. Being embedded into a random medium, dopant atoms or molecules are also inevitably subjected to positional and energetic disorder. Since the HOMO level in most organic semiconductors is deep and the gap separating LUMO and HOMO states is wide, energies of donor and acceptor molecules are normally well below LUMO and above HOMO, respectively. So we assume a double exponential density of states

$$g(\epsilon) = \frac{N_t}{k_B T_0} \exp\left(-\frac{\epsilon}{k_B T_0}\right) \theta(-\epsilon) + \frac{N_d}{k_B T_1} \exp\left(\frac{-\epsilon + E_d}{k_B T_1}\right)$$

where N_t and N_d are the concentrations of intrinsic states and dopant states, respectively, θ is unit step function, T_0 and T_1 are parameters indicating the width of intrinsic and dopant distributions, respectively, and E_d is the Coulomb trap energy [18]. Vissenberg and Matters pointed out that they do not expect the results to be qualitatively different for a different choice of $g(\epsilon)$, as long as $g(\epsilon)$ increases strongly with ϵ. Therefore, we assume that transport takes place in the tail of Gaussian distribution.

The equilibrium distribution of carriers, $\rho(\epsilon)$, is determined by the Fermi-Dirac distribution $f(\epsilon)$ as

$$\rho(\epsilon) = g(\epsilon) f(\epsilon) = \frac{g(\epsilon)}{1 + \exp\left[(\epsilon - \epsilon_F)/k_B T\right]}$$

and the Fermi-energy of this system is fixed by the equation for the carrier concentration n,

$$n = \int \frac{d\epsilon g(\epsilon)}{1 + \exp\left(\frac{\epsilon - \epsilon_F}{k_B T}\right)} = n_t + n_d \tag{2}$$

where

$$n_t = N_t \exp\left(\frac{\epsilon_F}{K_B T_0}\right) \Gamma(1 - T/T_0)\, \Gamma(1 + T/T_0)$$

$$n_d = N_d \exp\left(\frac{\epsilon_F - E_d}{K_B T_1}\right) \Gamma(1 - T/T_1)\, \Gamma(1 + T/T_1)$$

Here Γ is gamma function.

According to classical percolation theory [17], in a random Miller and Abraham network [7] the current flows through the bonds connecting sites. The conductivity of this system is determined when the first infinite cluster occurs. At the onset of percolation the critical number B_c can be written as

$$B_c = \frac{N_b}{N_s}. \tag{3}$$

$B_c = 2.8$ for a three-dimensional amorphous system, N_b and N_s are, respectively, the density of bonds and density of sites in this percolation system, which can be calculated as follows [19], [20].

$$N_b = \int d\mathbf{R}_{ij} d\epsilon_i d\epsilon_j g(\epsilon_i)\, g(\epsilon_j)\, \theta(s_c - s_{ij}) \tag{4}$$

$$N_s = \int d\epsilon g(\epsilon)\, \theta(s_c k_B T - \mid \epsilon - \epsilon_F \mid) \tag{5}$$

Here $\mathbf{R_{ij}}$ denotes the distance vector between sites i and j and s_c is the exponent of the conductance given by the relation [21]

$$\sigma = \sigma_0 \exp(-s_c). \tag{6}$$

Substituting $g(\epsilon)$, (4) and (5) into (3), we obtain an expression for B_c.

$$B_c = \frac{\kappa + p}{N_t \exp(\eta) + N_d \exp(\gamma)} \tag{7}$$

where

$$\kappa = \pi N_t^2 \psi^3 \exp(2\eta) + \pi N_d^2 \xi^3 \exp(2\gamma)$$

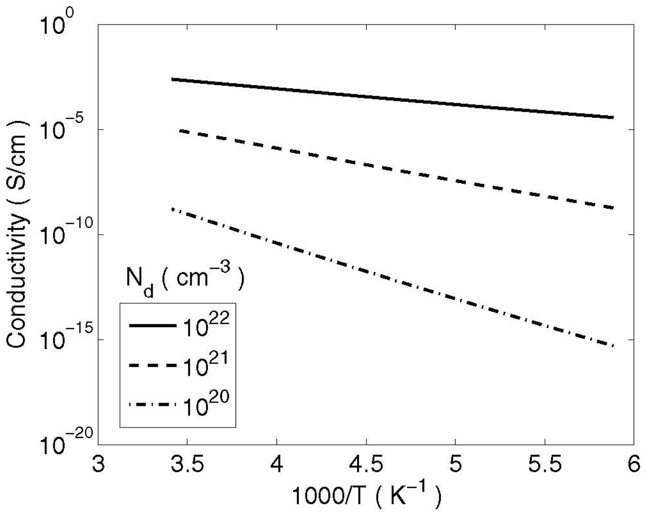

Fig. 1. Temperature dependence of the conductivity in disordered hopping system at different doping concentrations.

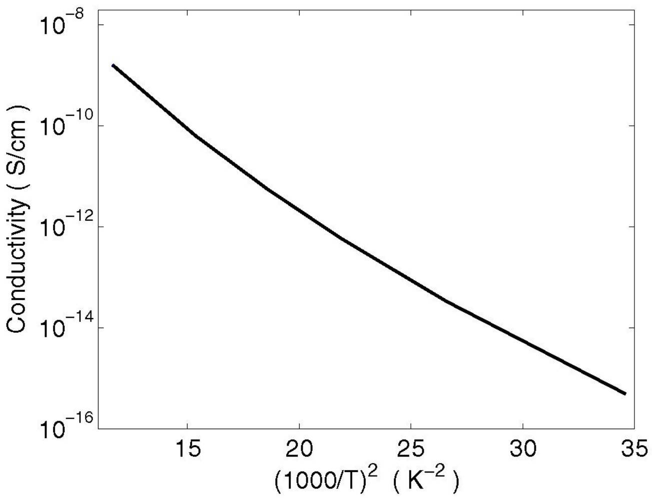

Fig. 2. The temperature dependence of the conductivity in organic semiconductors, plotted as $\log\sigma$ versus T^{-2}.

$$p = \frac{\pi}{4} N_t N_d \exp(\eta + \gamma) \left(\psi^{-1} + \xi^{-1}\right)^{-3}$$

and

$$\eta = \frac{\epsilon_F + k_B T s_c}{k_B T_0}, \qquad \gamma = \frac{\epsilon_F - E_d + k_B T s_c}{k_B T_1}$$

$$\psi = \frac{T_0}{4\alpha T}, \qquad \xi = \frac{T_1}{4\alpha T}$$

Equation (7) is obtained under the following conditions:

- the site positions are random,
- the energy barrier for the critical hop is large,
- and the charge carrier concentration is very low.

The exponent s_c is obtained by a numerical solution of (8).

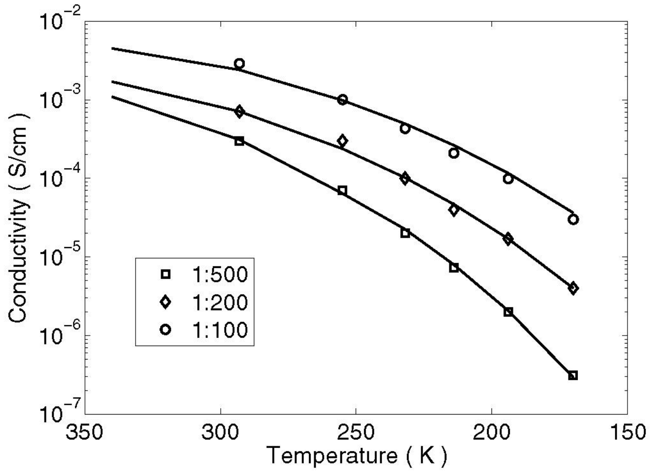

Fig. 3. Conductivity of doped ZnPc at various doping rates as a function of temperature. The lines represent the analytical model, experiments (symbols) are from [22].

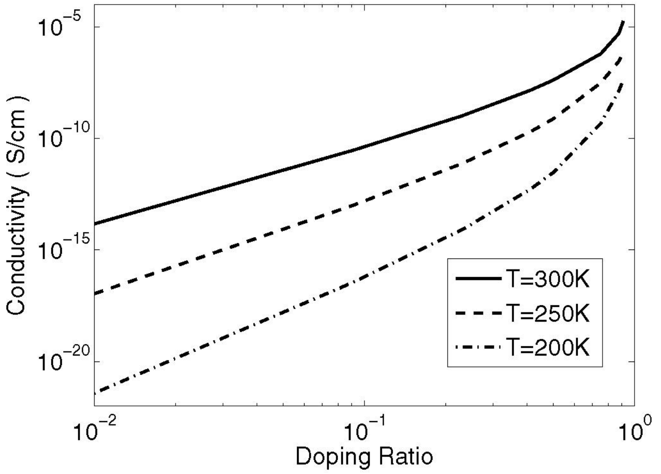

Fig. 4. Conductivity as a function of the doping ratio with temperature as a parameter.

III. RESULTS AND DISCUSSION

Fig. 1 illustrates the effect of the temperature dependence of the carrier conductivity for different doping concentrations. Parameters are $\alpha^{-1} = 0.37$Å, $E_d = 0.5$eV, $T_0 = 800$K and $T_1 = 400$K. The Arrhenius-like temperature dependence

$$\log\sigma \propto -E_A/k_BT$$

can be observed. The graph $\log\sigma$ versus T^{-2} is plotted in Fig. 2, where we observe a deviation from strick straight line. This is because at higher temperature, nearly all the carriers occupy the intrinsic states, so that dopants do not change the trap-free hopping relation of

$$\log\sigma \propto T^{-2}.$$

The doping process is quite efficient for ZnPc with dopant F4-TCNQ [22]. Fig. 2 shows the comparison between the measured conductivity of room temperature samples and the theoretical curves calculated from (7). The agreement is quite good. The fit parameters are the same as given in Fig. 1, which are taken from [22]. From Fig. 1 and Fig. 3 one can see that the doping efficiency dramatically increases with decreasing temperature. This can be explained by the notion that the activation energy of the equilibrium mobility of extrinsic carriers strongly increases with decreasing temperature.

This model also describes the relation between conductivity and doping ratio, which is defined as

$$\frac{N_t}{N_t + N_d}.$$

The calculated dependences are shown in Fig. 4 with the parameters $T_0 = 1000$K, $T_1 = 500$K, $E_d = 0.5$eV and $\sigma_0 = 1\times10^7$s/cm. The conductivity increases with doping ratio and temperature, but there is a transition in the conductivity of an organic semiconductors upon doping. It is manifested by a change in the slope of conductivity versus doping ratio. The effect is illustrated in Fig. 5. For low doping level, the conductivity increases with doping in nearly linearly. At higher doping levels, a superliner increase of conductivity with doping is observed. This transition has been interpreted in [18] in terms of broadening of the transport manifold due to enhanced disorder coming from the dopant.

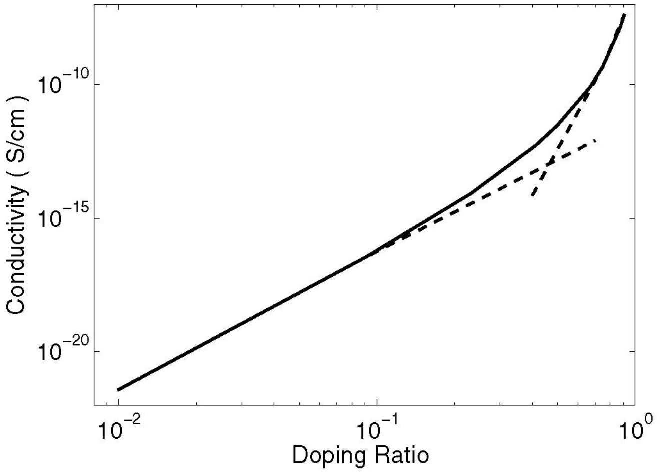

Fig. 5. Conductivity (T=200k) as a function of the doping ratio. The dashed line is to guide to the eye.)

Assuming a simple Arrhenius behavior

$$\sigma \propto \exp\left(\frac{-E_A}{k_BT}\right),$$

we can obtain the relation between activation energy E_A and doping ratio, as shown in Fig. 6. E_A decreases with doping ratio increasing, which means that less energy will be required for a carrier activated jump to neighboring sites. Fig. 6 also shows a transition between the two doping regimes which is visible as a change in the slope of E_A with doping ratio.

A comparison between our model and experimental data of doped PPEEB [23] is shown in Fig. 7. The input parameters

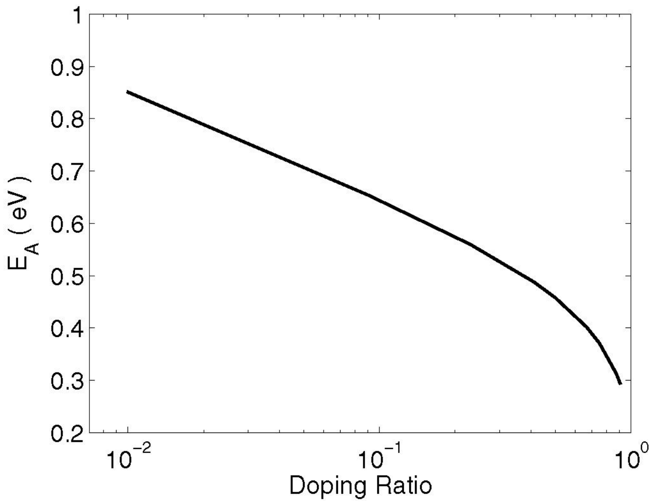

Fig. 6. Activation energy (E_A) as a function of the doping ratio.

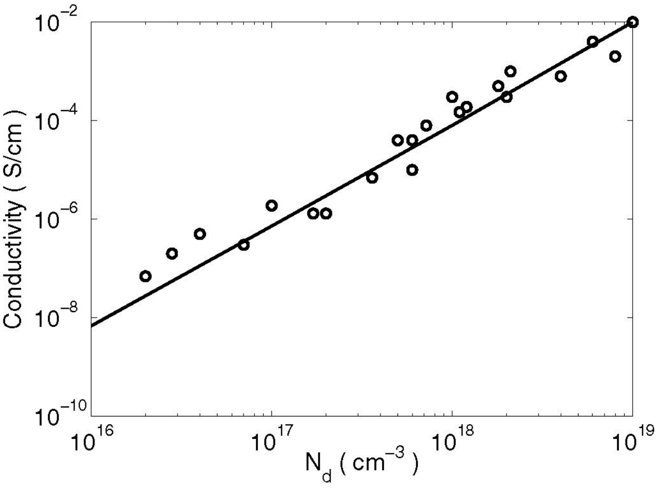

Fig. 7. Conductivity of PPEEB films versus the dopant concentration. The line represents the analytical model. Experiments (symbols) are from [23].

are $\alpha^{-1} = 6\text{Å}$, $E_d = 0.6\text{eV}$, $T_0 = 1000\text{K}$ and $T_1 = 500\text{K}$.

IV. CONCLUSION

We presented an analytical model to describe the doping dependent conductivity for organic semiconductors. This model can explain the Arrhenius type dependence of conductivity on temperature. Moreover, the doping efficiency increases with decreasing temperature. A transition in the conductivity of an organic semiconductor upon doping was observed. This model is shown to fit the experimentally observed dependence of conductivity on the dopant concentration.

ACKNOWLEDGMENT

We acknowledge financial support from the Austria Science Fund, project P16862-N02.

REFERENCES

[1] J. H. Burroughes, D. Bradley, A. Brown, R. Friend, P. Burn, and A. Holmers, “Point defects and dopant diffusion in silicon,” *Nature*, vol. 347, pp. 539–541, 1990.

[2] E. Mconwell, “Impurity band conduction in germanium and silicon,” *Phys.Rev*, vol. 103, no. 1, pp. 51–61, 1956.

[3] J. Blochiwitz, M. Pfreifer, T. Fritz, and K. Leo, “Low voltage organic light emitting diodes featuring doped phthalocyanine as hole transport material,” *Appl. Phys. Lett*, vol. 73, pp. 729–731, 1998.

[4] A. Nollau, M. Pfeiffer, T. Fritz, and K. Leo, “Controlled n-type doping of a molecular organic semiconductor: Naphthalenetetracarboxylic dianhydride (NTCDA) doped with bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF),” *J. Appl. Phys*, vol. 87, pp. 4340–4343, 2000.

[5] X. Zhou, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, and K. Leo, “Very-low-operating-voltage organic light-emitting diodes using a p-doped amorphous hole injection layer,” *Appl. Phys. Lett*, vol. 78, pp. 410–412, 2001.

[6] N. F. Mott *J.Phys*, vol. 34, p. 1356, 1956.

[7] H. Bassler, “Charge transport in disordered organic photoconductors,” *Phys.Stat.Sol.(b)*, vol. 175, pp. 15–56, 1993.

[8] N. F. Mott *J.Non-Cryst.Solids*, vol. 1, p. 1, 1968.

[9] J. R. Sheat, H. Antoniadis, and M. Hueschen, “Organic electroluminescent devices,” *Science*, vol. 16, pp. 884–888, 1996.

[10] A. J. Twarowski, “Photocurrent generation in zinc phthalocyanine films,” *J. Chem. Phys*, vol. 76, pp. 2640–2645, 1982.

[11] C. Ganzorig and M. Fujihira, “Improved drive voltages of organic electroluminescent devices with an efficient p-type aromatic diamine hole-injection layer,” *Appl. Phys. Lett*, vol. 18, pp. 4211–4213, 2000.

[12] B. Maennig, M. Pfeiffer, A. Nollau, and K. Leo, “Controlled p-type doping of polycrystalline and amorphous organic layers,” *Phys.Rev.B*, vol. 64, pp. 1952081–1952089, 2001.

[13] M. Maitrot and B. Boudjema, “Molecular material-based junctions: Formation of a schottky contact with metallophthalocyanine thin films doped by the cosublimation method,” *J. Appled. Phys*, vol. 60, pp. 2396–2400, 1986.

[14] C. Godet, “Variable range hopping revisited: the case of an exponential distribution of localized states,” *J.Non-Cryst.Solids*, vol. 299, pp. 333–338, 2002.

[15] O. Rubel, S. D. Baranovskii, and P. Thomas, “Concentration dependence of the hopping mobility in disordered organic solids,” *Phys.Rev.B*, vol. 69, pp. 0142061–0142065, 2004.

[16] C. P. Jarrett, R. H. Friend, A. R. Brown, and D. M. de Leeuw, “Field effect measurements in doped conjugated polymer films: Assessment of charge carrier mobilities,” *J. Appl. Phys*, vol. 77, pp. 6289–6294, 1995.

[17] V.Ambegokar, “Hopping conductivity in disordered system,” *Phys. Rev. B*, vol. 4, no. 8, pp. 2612–2620, 1971.

[18] Y. Shen, K. Diest, M. H. Wong, B. R. Hsieh, D. H. Dunlap, and G. Malliaras, “Charge transport in doped organic semiconductors,” *Phys. Rev. B*, vol. 68, no. 8, pp. 0812041–0812044, 2003.

[19] M. C. J. M. Vissenberg and M. Matters, “Theory of the field-effect mobility in amorphous organic transistors,” *Phys. Rev. B*, vol. 57, no. 20, pp. 12964–12967, 1998.

[20] P. N. Butcher, *Linear and Nonlinear Electron Transport in Solids*. New york, USA: Plenum, 1976.

[21] M. Sahimi, *Applications of Percolation Theory*. London, Uk: Taylor Francis, 1994.

[22] B. Maennig, M. Pfeiffer, A. Nollau, X. Zhou, and K. Leo, “Controlled p-type doping of polycrystalline and amorphous organic layers,” *Phys. Rev. B*, vol. 64, pp. 1952081–1952088, 2001.

[23] B. A. Gregg, S. G. Chen, and H. M. Branz, “On the superlinear increase in conductivity with dopant concentration in excitonic semiconductors,” *App. Phys. Lett*, vol. 84, pp. 1707–1709, 2004.