Analytical model of Energy Level Alignment at Metal-Organic Interface facilitating Hole Injection

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***Abstract*—An analytical description of energy level alignment at metal-organic interface based on a detailed electrostatic model and exponential density of states is presented here. The calculated alignment between the Fermi energy of electrode and the organic transport energy shows good quantitative agreement with the proposed numerical electrostatic model and experimental data, indicating that the analytical model can well describe the material disorder and carrier density. More important, the simulations highlight that the electrode with high effective work functions and the organic material with large dielectric constant can facilitate the hole injection from metal to organic. Finally, the Gaussian distribution density of states has compare to the exponential model, confirmed the accuracy of the analytical description for energy level alignment.**

Keywords—Metal-organic interface; Energy level alignment; Exponential density of states; Electrostatic model.

I. Introduction

In organic based electronics, such as light-emitting devices, thin film transistors, and bulk hetero-junction solar cells, which show great potential in application of flexible, transparent, and large area electronics, device performance and lifetime rely on the properties of the interface between metal and organic[1, 2]. Even though many applications are in an advanced stage with some already commercially available, no reliable interface design criteria to device manufacturers at present.

Since the process of charge injection ultimately determines the performance of organic devices, one of the key issues for organic electronic technologies is the understanding of the energy level alignment at interfaces involving semiconductor and metal. For example, the energy level alignment at the interfaces of organic and metal in schottky junction based organic solar cells is critical for efficient charge separation, and significantly affects the open-circuit voltage as well[3, 4]. Central to this issue is the problem of the organic level alignment at these interfaces: the relative position of the energy levels of the metal and the organic material once the interface is formed determines the injection barrier at the metal organic interface. Although inorganic semiconductor interfaces offer inspiration for understanding the energy level alignment, the topic at metal organic interfaces is still not fully understood.

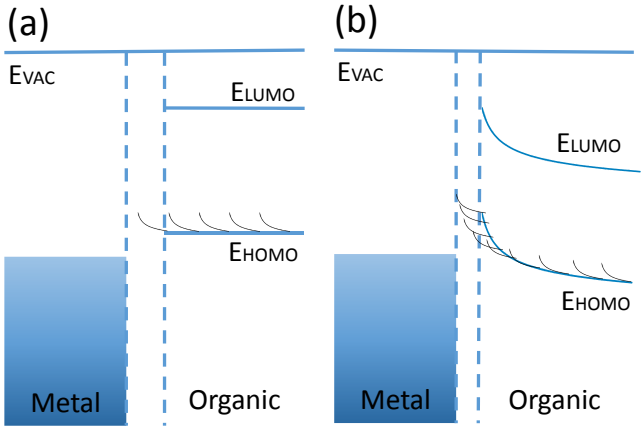

Fig. 1 (a) Schematic energy level diagram at organic/electrode interface, example of a possible initial situation for the organic and metal before contact. (b) Final energy level alignment after contact.

There are many outstanding works about the energy level alignment developed by Vasquez et al., Blakesley et al., Greiner et al., as well as Ley et al. They mentioned that contact layer can facilitate the emission of electrons and holes from the cathode or anode into the organic stack. The characteristic quantities for these contacts are the emission barrier for electrons and holes which the carriers have to overcome when entering the transport levels of the adjacent organic molecule.

Recently, a detailed numerical electrostatic model, which could accurately reproduce the alignment between the electrode Fermi energy and the transport states in the organic semiconductor, was proposed by M. Oehzelt[5]. To acquire an analytical model, we rewrite the energy level alignment using the exponential density of states based on previous numerical model. More narrowly, an analytical description of energy level alignment at metal-organic interface based on a detailed electrostatic model and exponential density of states is presented here. The calculated alignment between the electrode Fermi energy and the organic transport energy shows good quantitative agreement with the proposed numerical electrostatic model and experimental data, indicating that the analytical model can well describe the material disorder and carrier density. More important, the simulations highlight the

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high effective electrode work functions and large organic dielectric constant facilitate the hole injection from metal to organic. Finally, the Gaussian distribution density of states has compare to the exponential model, confirmed the accuracy of the analytical description for energy level alignment.

II. MODELING

In Fig.1a, a typical situation for the energetic alignment of all relevant electronic states is sketched schematically. In such situation, charge carriers encounter energy barrier, if they are to be injected and that for extraction corresponding energy losses occur. However, for a specific material pair, the situation sketched in Fig.1a is found unsatisfactory, the obvious strategy is to reduce barriers by either moving Fermi energy of metal towards the HOMO or LUMO[6, 7].

The work function of the organic film defined by the energy difference between the Fermi level and the vacuum level outside the organic semiconductor film. The work function is actually higher than the ionization energy of organic semiconductor, where electrons reside at energies above Fermi energy before charge equilibration. It is clear that in the course of establishing a common electron chemical potential, charge will flow across the interface[8, 9].

For disordered organic semiconductors, charge carriers move via incoherent tunneling between spatially and energetically distributed localized states, and the Gaussian density of states is usually assumed to describe the energy distribution of localized states in organic semiconductor as[10, 11]

$$g(E) = \frac{N_t}{\sqrt{2\pi}\sigma} exp\left(-\frac{E^2}{2\sigma^2}\right). \quad (1)$$

where σ is Gaussian standard deviation, N_t is the number of states per unit volume, E is the energy.

To quantify the amount of transferred charge in the general case, we then calculate the charge density $\rho(z)$,

$$\rho(z) = en\int_{-\infty}^{+\infty} dE g\big(E + eV(z)\big) f(E, E_F), \quad (2)$$

where e is the elementary charge, n is the number of molecules per unit area.

The electrostatic potential across the organic semiconductor film, $V(z)$, is first set to zero for calculating an initial guess of the charge density via equation 2. Once known, this $\rho(z)$ serves to find the next $V(z)$, which we obtain by numerically solving the generalized one dimensional Poisson equation

$$\frac{\partial^2 V}{\partial z^2} = -\frac{\rho(z)}{\varepsilon}, \quad (3)$$

We change the Poisson equation to

$$\int_{\frac{\partial V}{\partial z}|z=0}^{\frac{\partial V}{\partial z}|z=a} \frac{\partial V}{\partial z} d\left(\frac{\partial V}{\partial z}\right) = -\int_{V|z=0}^{V|z=a} \frac{\rho(V(z))}{\varepsilon} dV \quad (4)$$

We combine the equation 2, 4 with Fermi-Dirac distribution,

$$\frac{1}{2}\left(\frac{\partial V}{\partial z}\right)^2 \begin{cases} \frac{\partial V}{\partial z}|z=a \\ \frac{\partial V}{\partial z}|z=0 \end{cases} =$$
$$-\int_0^V \frac{en}{\varepsilon}\int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi}\sigma} \frac{1}{1+\frac{1}{2}exp\left(-\frac{E-E_F}{k_BT}\right)} exp\left(-\frac{(E-E_h+V)^2}{\sigma^2}\right) dV, \quad (5)$$

where E_h is the HOMO energy level, with the discrete difference method on a variable grid, using the second order, central difference scheme with mixed $V(0) = 0$ and $V'(d) = 0$ boundary conditions, where d is the total thickness of the considered organic film and ε is the dielectric constant.

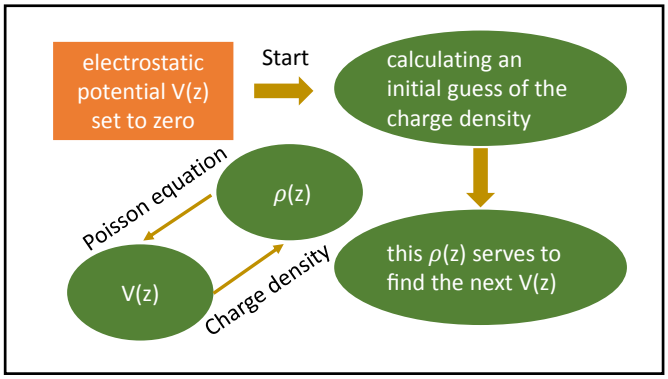

Fig.2. The detailed flow chart of numerical electrostatic model.

According to the boundary conditions $V'(d) = 0$, we define the ${F_0}^2$ as

$${F_0}^2 = \left(\frac{\partial V}{\partial z}\right)^2|_{z=0} =$$
$$\frac{2en}{\varepsilon}\int_0^V \int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi}\sigma} \frac{1}{1+\frac{1}{2}exp\left(-\frac{E-E_F}{k_BT}\right)} exp\left(-\frac{(E-E_h+V)^2}{\sigma^2}\right) dV\, dE, \quad (6)$$

and

$$\frac{\partial V}{\partial z} = \sqrt{{F_0}^2 - \frac{2en}{\varepsilon}\int_0^V \int_{-\infty}^{+\infty} \frac{1}{\sqrt{2\pi}\sigma} \frac{1}{1+\frac{1}{2}exp\left(-\frac{E-E_F}{k_BT}\right)} exp\left(-\frac{(E-E_h+V)^2}{\sigma^2}\right) dV dE} \quad (7)$$

The detailed flow chart of numerical electrostatic model is shown in Fig.2. These numerical electrostatic method is similar as M. Oehzelt.

To obtain an analytical model, we use an exponential form instead of gussian one[12].

$$g(E) = \frac{N_t}{k_BT_0} exp\left(\frac{E}{k_BT_0}\right). \quad (8)$$

where T_0 is the characteristic temperature which represents material disorder.

$${F_0}^2 = \left(\frac{\partial V}{\partial z}\right)^2|_{z=0} = \frac{2en}{\varepsilon} \frac{\frac{\pi T}{T_0}}{\sin\left(\frac{\pi T}{T_0}\right)} \frac{k_BT_0}{q} \exp\left(-\frac{E_F}{k_BT_0}\right) \times$$
$$\left(1 - \exp\left(-\frac{qV(max)}{k_BT_0}\right)\right) \quad (9)$$

$$\int \frac{dV}{\sqrt{\frac{2en}{\varepsilon}\frac{\pi T/T_0}{\sin(\pi T/T_0)}\frac{k_BT_0}{q}\exp(-\frac{E_F}{k_BT_0})\exp(-\frac{qV(x)}{k_BT_0})}} = z \quad (10)$$

We get the analytical model as

$$z = \frac{1}{F_0}\frac{2k_BT_0}{q}\left(\exp\left(\frac{qV(x)}{2k_BT_0}\right) - 1\right) \quad (11)$$

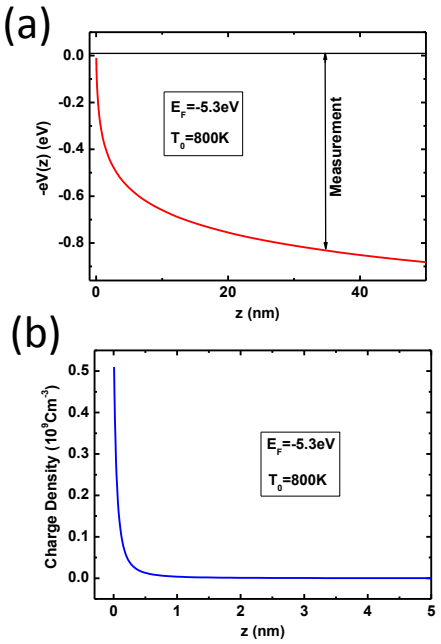

Fig.3. (a) Calculated electron potential energy –eV(z) within a thickness of 50nm organic film. (b) Calculated charge density within a 5nm film. The parameters are ε=3.6, E_F=-5.3eV and T_0=800K, in addition, surface potential sensitive experimental methods (UPS or KPFM) only determine the total electron potential energy drop across the entire organic film.

III. Results and Disscussion

The details of the model were illustrated in Figure 1. For disordered organic semiconductors, charge carriers move via incoherent tunneling between spatially and energetically distributed localized states, and the Exponential density of states is usually assumed to describe the energy distribution of localized states in material systems. In Fig. 1a, a typical situation is sketched schematically for the energy level alignment of metal and organic before contact. When the metal nearly close to organic, an injection barrier forms at this interface for Fig. 1b. According to Poisson equation and the charge density expression, the electron potential energy –eV(z) can be analytic presented as equation (11) within a thickness of 50 nm organic film. The simulation results of electron potential energy distribution show in Fig. 3(a). The input parameters are ε=3.6, E_F=-5.3eV and T_0=800K, in addition, surface potential sensitive experimental methods (UPS or KPFM) only determine the total electron potential energy drop across the entire organic film[13-15]. The charge density drastically decrease within first several nanometer like Fig. 3(b), while approaching to the bulk of organic. The electron potential energy drop is expected to decrease with the reduction of material disorder degree as eliminating defects within the organic and the increase the charge density as giving additional light exposure[16-18]. The proposed model reproduce the correct relationship for the energy level alignment in Fig. 4. Furthermore, the calculated electron potential energy eV(z)

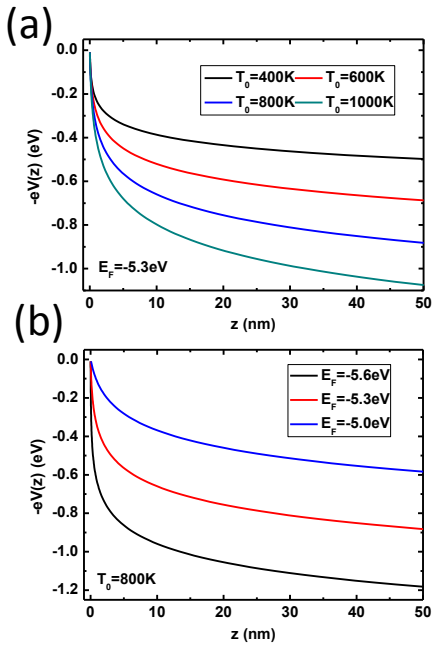

Fig. 4 (a) Calculated electron potential energy within a thickness of 50nm organic film at different disorder degree. (b) Calculated electron potential energy distribution for a series of Fermi level energies.

with different organic dielectric constant is shown in Fig. 5(a), and the well fitted curves of calculated electron potential energy distribution between our exponential analytical model and the Gaussian based numerical model.

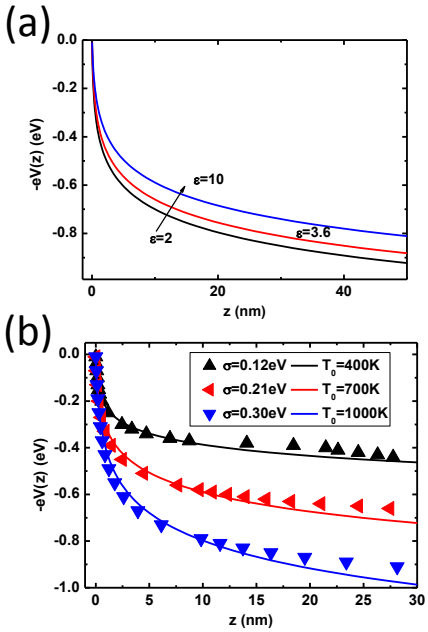

Fig. 5 (a) Calculated electron potential energy –eV(z) with different organic dielectric constant. (b) Comparison of calculated electron potential energy distribution for exponential and Gaussian DOS.

IV. CONCLUSIONS

In conclusion, an analytical model of the energy level alignment is presented here. The simulations highlight the high effective electrode work functions and large organic dielectric constant facilitate the hole injection from metal to organic. Finally, the Gaussian distribution density of states has compare to the exponential model, confirmed the accuracy of the analytical description for energy level alignment.

V. ACKNOWLEDGEMENTS

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