Carrier Accumulation in Organic Heterojunctions
Controlled by Polarization

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Abstract

We present a heterojunction theory of ultrathin organic multi-layered devices, which is the revision of our previous work. Their characteristic feature is the generation of conductive space charge region in the insulating neutral dielectric region under the bias voltage application, while the insulating space charge region is generated in the conductive neutral region in the case of semiconductors. We propose the concept of quasiconductor to describe these features. From the theory, the capacitor equation of mobile carriers is given, which is an equivalent equation of the Mott-Schottky equation in semiconductor physics. Because the organics are dielectrics, the dynamics are controlled cleverly by polarization. The theory gives a relation among the applied voltage, carrier accumulation, mobility, and carrier density, which enables the in-situ simultaneous evaluation of mobility and the carrier density of ultrathin organic multi-layered devices. The concept of quasiconductor is a missing link between organic electronics and the semiconductor physics.
Introduction

It had been known that crystals of organic materials were able to become semiconductors since the 1940s [1]. After two innovations of the discovery of conductive polymers in 1976 [2] and the invention of ultrathin organic multi-layered devices in 1986 [3], organic electronics have achieved great success in scientific and industrial fields. As of 2020, Organic Light Emitting Diode (OLED) has achieved the greatest success as a display device in the field. Besides, Organic Field Effect Transistor (OFET) as a fundamental technology for printed electronics and Organic Solar Cell (OSC) as a low-cost flexible energy source are being actively researched. While organic electronics are rapidly expanding in the market, our understanding of their operational dynamics is less developed. Even though our understanding of electronic states in molecular systems deepens more and more, the mysteries of device physics get deeper and deeper [4-6]. The delocalized band structure in inorganic semiconductor crystals has been reinterpreted in terms of the localized levels of HOMO and LUMO in molecules, and the device theory established by the band theory has been used to explain organic device properties. Surprisingly, despite the patchwork theory in different material groups with a different electronic nature, the performance of organic devices can be explained quantitatively to some extent [7, 8]. What are the reasons for this
success? Or are we just gorging ourselves on glory under phantom prosperity? The development of organic electronics has been guided by the semiconductor theory, but the fraying of the semiconductor theory would be a burden for the next stage of developments in organic electronics.

We have analyzed ultrathin organic multi-layered devices (UOMD) using impedance spectroscopy and reported that device physics in them is quite distinct from that of semiconductor devices [9-12]. One of the characteristic features of UOMD is the carrier accumulation. Because the organics are dielectrics, OLEDs are considered as capacitors below the current threshold voltage when the accumulation layer and the non-accumulation layer are considered as the electrode and the polarization layer, respectively. The number of charges per area stored in the accumulation layer for applied voltage V is \( Q = \epsilon V \), where \( \epsilon = \epsilon / l \) with \( l \) the thickness of the non-accumulation layer [10, 11]. For a typical OLED such as ITO/\( \alpha \)-NPD/Alq3/LiF/Al, holes accumulate in the HT layer below the current threshold voltage. Because proper semicircles appear in the Modulus Cole-Cole plots, the holes distribute in the whole HT layer uniformly once the layer is accumulated fully [9]. It is in contrast with the case of usual capacitors with an insulating polarization layer and metal electrodes, where the real charges are stored within a thin layer in the electrode.

In the previous articles, we reported that there was a finite external source of the
accumulated carriers because the conductivity of the accumulation layer was inversely proportional to the corresponding layer thickness [9, 10]. However, this is not correct. Since the stored carriers are the charged charges to the MIS capacitor, those number are determined by the geometry of the device and there is no need to consider an independent carrier source. We solved the simultaneous equations of the Poisson equation and the continuity equation to evaluate the carrier distribution. We gave a relation between the thickness of the accumulated layer and the applied voltage. However, the sign of the potential of the accumulated layer and the treatment of boundary conditions were wrong. We reconsider the boundary conditions in detail to take into account the contribution of the polarization to the accumulation. The revised theory gives the same mobility equation derived in the previous article.

**Theory and discussion**

We start with a summary of the carrier generation in quasiconductors. The quasiconductor is a polaron hopping conductor with the charge-neutral insulator phase and the external carrier source [10, 11]. The semiconductor is a band system, the electron wave functions of which delocalize over the crystal as Bloch states. On the other hand, the electron wave functions of small molecular organics in the amorphous states localize in each molecule because the phases
of wave functions of neighboring molecules cancel statistically due to the disorder. Even though the wave functions localize on the molecule, there are finite overlaps of HOMOs and LUMOs among the neighboring molecules, which promote the carrier transport between molecules by the hopping process. Remember that the excitation from HOMO to LUMO itself does not generate a carrier. The excitation within the molecule generates a neutral exciton, in which the electron and hole are bounded. Unlike the excitation in the semiconductors, where excited electrons enter the delocalized conduction band and become a carrier, the excitation in the organics generates only a neutral excited state that cannot contribute to conduction. However, when the organic contacts with a metal, the work function of which locates within the HOMO and LUMO, the electron can diffuse through the metal/organic interface without energy loss as shown in Fig.1. After the diffusion of the electron, cations or anions are left in the organic. When the externally applied voltage cancels the internal electric field and the potential in the organic becomes flat, the hole in the HOMO or the electron in the LUMO can be exchanged with the neighboring neutral molecules without energy loss. The isolated holes or electrons diffuse into the organic as carriers. Above the current threshold voltage, the current density obeys to the Shockley equation with the ideality factor of around 1.5 to 2 at low voltage in the case of diodes, [13, 14]. It suggests that it is governed by some thermal excitation process consistent with the excitation from HOMO
to LUMO. It seems that it was assisted by the deep traps, the process of which is similar to the SRH process as in semiconductors [15]. However, the SRH model was developed for the band systems. Careful treatment will be necessary for further discussion. At higher voltage, the carrier supply will be switched from the diffusion process to the direct electron/hole injection from the electrode metal or transport limited processes in the bulk. In the present article, we concentrate the discussion mainly on the static behavior of the carrier dynamics below the current threshold voltage. The carrier distribution is governed by the balance between the diffusion current and the drift current, the underlying concept of which is similar to that of the Schottky junction of semiconductors. However, one must remember that the charged state of semiconductors is the insulator and that of the organics is the conductor. The roles are switched. From this duality in the carrier transport of semiconductors and organics, we proposed a new classification of quasiconductor for the organic conductors in opposition to semiconductors [10, 11].

The equations governing the balance between the diffusion current and the drift current due to the space charge are the Poisson equation and the continuity equation [10].

$$\Delta \phi = - \frac{qN}{\varepsilon}.$$ \hspace{1cm} (1)

$$0 = \sigma E - q D \nabla N.$$ \hspace{1cm} (2)

With $q$ the elementary charge, $\varepsilon$ the permittivity, $\sigma = qN\mu$ the conductivity, $\mu$ the mobility, $N$
the carrier density, and \( D \) the diffusion coefficient. For one dimensional coordinate, the following equation is obtained after an integration.

\[
A = \frac{\mu}{2D} \left( \frac{d\phi}{dx} \right)^2 + \frac{d^2\phi}{dx^2}.
\]  

(3)

This equation has solutions as

\[
\phi(x) = -\frac{2D}{\mu} \ln \left( \cosh \left( \frac{\mu A}{2D} (x - x_0) \right) \right) + \phi_0(x).
\]  

(4)

\[
\frac{d\phi}{dx} = -\sqrt{\frac{2DA}{\mu}} \tanh \left( \frac{\mu A}{2D} (x - x_0) \right) + \frac{d\phi_0(x)}{dx}.
\]  

(5)

\[
\frac{d^2\phi}{dx^2} = -\frac{qN}{\varepsilon} = A \cosh^2 \left( \frac{\mu A}{2D} (x - x_0) \right).
\]  

(6)

Here, \( \phi_0(x) \) are the solutions satisfying \( \Delta \phi_0(x) = 0 \). For one dimensional system, \( \phi_0(x) = ax + b \). \( A \) is redefined as \( A = qN_0/\varepsilon \). \( D \) and \( \mu \) are connected by the Einstein relation, \( 1 = qD/\mu kT \). In general, this value can be larger than 1 [16, 17]. We define the following values,

\[
\zeta = \frac{qD}{\mu kT},
\]  

(7)

\[
\lambda_D = \sqrt{\frac{2e kT}{q^2 N_0}}
\]  

(8)

\[
\lambda_D = \sqrt{\frac{2e D}{q^2 N_0 \mu}} = \sqrt{\zeta} \lambda_{D0},
\]  

(9)

\( \lambda_D \) is the generalized Debye length in a dielectric material with permittivity \( \varepsilon \). Here, we assume that the hole density is sufficiently low that the Debye length is sufficiently larger than the HT layer thickness. Under this assumption, we can simplify the equations from eq.(4) to eq.(6) as

\[
\phi(x) = -\frac{qN_0}{2e} (x^2 + mx + n).
\]  

(10)
\begin{align}
E(x) &= \frac{qN_0}{2\varepsilon}(2x + m). \\
N(x) &= qN_0. \tag{12}
\end{align}

Here, m and n are the numerical constants that are determined from the boundary conditions.

If the Debye length is sufficiently larger than the organic layer, the abrupt distribution approximation that is popular in the analysis of semiconductor junction is effective for those devices [15]. We will discuss the validity of the approximation of large Debye length later.

Next, we discuss the multi-layered devices. The carrier behavior in organic multi-layered devices has been studied in detail by displacement current method and impedance spectroscopy [9, 12, 18-22]. The organic materials used in these devices are insulating dielectrics with few carriers in the neutral state. When a bias voltage is applied to the devices, stepwise carrier injection is observed in the multi-layered device. Part of the layers is observed to shift from the insulator to the conductor at the negative bias side of the threshold voltage before the start of DC current flow. The conductive region becomes progressively thicker as the voltage increases and saturates. It is difficult to assume that the organic material itself ionizes and the excess charge is released from the molecule into the bulk as a carrier with keeping the charge-neutrality condition under the applied voltage. The carriers will be supplied from the metal by the above-mentioned process so that the space charges violate the neutral insulator phase. The accumulation voltage is the offset of the start voltage of the
accumulation from the built-in potential. The accumulation voltage is known also as the giant surface potential (GSP) [19-21]. GSP represents the polarization mismatch appearing at the heterointerface. It is considered as a spontaneous polarization. We consider two-layer organic devices of dielectrics without real charges within them. Figure 2 are the potential and charge distribution diagrams. Only the layer I is assumed to have the spontaneous polarization. The thick blue lines show the real charges and the thick yellow lines are the imaginary charges appearing at the edges of the polarized layers. The thick black lines outside the devices show the externally applied voltage. The broken and thick red lines within the devices show the polarization and the internal potential that is the sum of the polarization and the externally applied electric field. When the device is opened, the spontaneous polarization in the layer I causes polarization in layer II because there are no real charges at the interface between the organic layers as in Fig.2(a). When a bias voltage is applied to the device, the real charges increase on the electrode surface until the internal potential becomes flat at the accumulation voltage $V_a$ as in Fig.2(b). When the potential in layer II becomes flat, carriers start to accumulate in the layer as space charges. During the accumulation, the edges of the accumulation layer are equipotential, and the space charge accumulation accompanies the decreases of the polarization and the interface charges of the layer II as in Fig.2(c). When the applied voltage exceeds the built-in potential (if the electrode metals are different, there is a
potential difference), the internal electric field exceeds over the spontaneous polarization field that is the stopping force of the carrier drift. DC current flow starts in the case that the layer I is a quasiconductor as in Fig.2(d). On the other hand, if the layer I is an insulator, the number of carriers accumulated in layer II will increase monotonically as the bias voltage further increases. This difference is observed in the Modulus spectra of an OLED and an OFET. In the case of an OLED, ITO/α-NPD/Alq3/LiF/Al, a gradual accumulation in the HT layer of α-NPD was observed to start at a voltage sufficiently lower than the built-in potential. The accumulation saturated within a small voltage difference less than 1V (depending on the Alq3 thickness) and the relaxation frequency of the fully accumulated region did not change above the voltage of saturation [9]. On the other hand, the Modulus spectroscopy of the OFET, which has the structure where the ET of an OLED is replaced by the insulator, also showed that there was a relaxation peak corresponding to the full accumulation in the organic layer. The thickness of the accumulated region, the height of the relaxation peak of ImM was nearly constant and its relaxation frequency increased monotonically as the gate voltage up to 30V [23]. These behaviors are consistent with the above discussion. However, there remains a problem what governs the gradual accumulation and how to evaluate the carrier density. We must assume fixed interface charges at the heterointerface to model the gradual accumulation consistent with the experimental results. The real charges at the organic/organic interface are
not possible from the spontaneous polarization due to the molecular orientation of polarized molecules. Charge trap by defects or some charge transfer reaction at the interface will be necessary [24-26]. We discuss it in the following.

We consider the charge distribution of hole accumulation in a simple two-layer device with a negative interface charge at the HT/ET interface. The coordinates are defined as in Fig.3, where the origins of the position and the potential are set at the HT/ET interface. At the accumulation voltage $V_a$, where holes start to accumulate in HT, the energy level of HT is flat and there is an internal electric field in ET. The internal electric field is compensated by the positive interface charges at the anode side as in Fig.3(a). When the bias voltage increases, the positive interface charges at the anode decreases. At the same time, the negative charges on the opposite side decrease. When the interface charges are fixed ones, the decrease of the negative charges are compensated by the increase of positive charges, the hole accumulation in HT as in Fig.3(b). The number of accumulated carriers and the thickness of the accumulated region determined from it are linked by the applied voltage through the number of the interface charges. Because a net current flow is absent under the excess bias voltage from the flat level condition, an inverse electric field is generated by the polarization in the non-accumulated region of the HT to offset the incremental space charge potential due to hole accumulation, and an equipotential state is maintained at both ends of
the HT. The potentials in the accumulated region (II) and the non-accumulated region (III) are written as follows,

In region II

\[
\phi_{II}(x) = -\frac{qN_0}{2\varepsilon_1}x(x - a). \tag{13}
\]

\[
E_{II}(x) = \frac{qN_0}{\varepsilon_1}(2x - a). \tag{14}
\]

In region III

\[
\phi_{III}(x) = -\frac{qN_0}{2\varepsilon_1}d(d - a) - E_{III}(d)(x - d). \tag{15}
\]

\[
E_{III}(x) = E_{II}(d) = \frac{qN_0}{2\varepsilon_1}(2d - a). \tag{16}
\]

Because \( \phi_{II}(0) = \phi_{III}(t) = 0 \), the following relationship holds.

\[
a = 2t - \frac{d^2}{t}. \tag{17}
\]

Here, \( t \) and \( d \) are the thicknesses of the HT layer and the accumulated region. There appear interface charges at the cathode to compensate for the discontinuity of the electric field at the HT/cathode interface.

\[
\varepsilon_1\phi_{III}'(t) = -\frac{qN_0}{2}(2d - a). \tag{18}
\]

From the Gauss theorem, the electric field at the HT/ET interface satisfies the next equations.

\[
\varepsilon_1\phi_{II}'(0) = -qN_0d - \varepsilon_1\phi_{III}'(t) = \frac{qN_0(2td - a^2)}{2t}. \tag{19}
\]

\[
\varepsilon_1\phi_{II}'(0) + \varepsilon_2\frac{V}{l} = \sigma_s. \tag{20}
\]

Here, \( \sigma_s \) is the fixed interface charges at the HT/ET interface and \( l \) is the thickness of the
ET layer. The permittivity of the ET, $\varepsilon_2$, is distinguished from that of the HT, $\varepsilon_1$. We define the full accumulation voltage $V_f$, where the thickness of the accumulated region coincides with $t$. We obtain the accumulation equation equivalent to the Mott-Schottky equation as

$$\sigma_s \frac{(d-t)^2}{t^2} = \varepsilon_2 \frac{V-V_f}{l}. \quad (21)$$

$$qN_0t = 2\sigma_s. \quad (22)$$

Because the thickness of the accumulated region is zero at the accumulation voltage, $V_a - V_f = \sigma_s l / \varepsilon_2$. It is shown that the number of accumulated carriers at the full accumulation state is governed by the geometrical configuration of the device. At the same time, the voltage difference between the start and the full state of accumulation, and the carrier density are governed by the fixed interface charges at the HT/ET interface. Around the accumulation voltage, where $d<<t$, eq. (21) is written as

$$qN_0d = \varepsilon_2 \frac{V-V_a}{l}. \quad (23)$$

From the obtained $N_0$, the mobility equation is given again as [10]

$$\mu = \frac{a}{qN_0} = \frac{2\pi\varepsilon_f}{qN_0}. \quad (24)$$

Here, $f$ is the relaxation frequency of the fully accumulated HT layer that is evaluated from the Modulus spectrum. $\varepsilon_1$ and $\sigma$ are the permittivity and the conductivity of the layer.

Equation (23) and (24) are the same equations as those derived in the ref. (10) and (11).

Equation (23) is the capacitor equation with the permittivity of $\varepsilon_2$ and the thickness of the
polarization layer of \( l \). It might not be surprising that the thickness of accumulated region “during” accumulation could be written by the capacitor equation because the equation was derived under the consideration of charge accumulation in dielectric materials. However, even though the \( N_0 \) was determined by the capacitance of the device and the thickness of the accumulation layer at the full accumulation state, it was not obvious why the same accumulation density is not achieved in the partially accumulated state. The present model shows that the fixed interface charges control the carrier density during the accumulation. At the full accumulation voltage, the same number of the fixed interface charges at the HT/ET interface appears at HT/cathode interface and the accumulated charges in the HT layer cancel them as in Fig.3(c). The considerations about the boundary conditions were not appropriate in the ref. (10) and the coincidence is only an accident. Within the framework of the present model of accumulation, the fixed interface charges and the spontaneous polarization governing GSP are independent of each other. Their origins are future problems.

Finally, we discuss the Debye length. We have obtained the hole density in the HT layer of OLEDs as \( 10^{16} \text{cm}^{-1} \), where the thicknesses of the polarization layer and the accumulation layer are 50 and 85nm (the derivation of the mobility equation used in the reference was wrong, but the equation itself was valid coincidentally) [11]. The Debye length calculated by eq. (8) is about 30nm. This value is shorter than the thickness of the HT layer.
of the used OLEDs. Considering the effect of Debye shielding in dielectric materials, non-uniform carrier distributions are expected in normal OLED film thickness configurations. However, the shapes of semicircles of the Modulus Cole-Cole plot look proper circles in the situation of the full accumulation so that the carrier localization in the vicinity of the electrode seems absent within the layer. A possibility is pointed out that \( \zeta \) the ratio of the diffusion constant to the mobility can be larger than unity in disordered materials [16, 17]. If we accept it, \( \zeta \) is at least larger than 10 in the OLEDs used for the evaluation of carrier density. In the case of OFET with a 500nm insulator layer and a 40nm organic layer, the height of the ImM of the relaxation peak of the organic layer which represents the effective thickness of the conductive region does not show obvious change up to the gate voltage of 30V [23]. From it, \( \zeta \) is estimated at over 100. There are reports that current-voltage dependence should be explained by small values of \( \zeta \) [13, 17]. Their analysis is based on the dynamic flow of carriers in semiconductors, while our analysis is based on the static behavior of carriers without considering the band structure. We do not necessarily believe that there is any necessity for the two to coincide. Under the present quasiconductor model, the shape of the Modulus spectrum is critical for the evaluation of \( \zeta \). It can be evaluated directly from the distortion of the shape of the Modulus spectrum, using devices with the thinner accumulation layer, the thicker polarization layer, and the higher gate voltage. Reliable values of the
diffusion coefficient are necessary for reliable device simulation. Further theoretical and experimental investigations are expected to develop a consistent picture of carrier dynamics.

**Conclusion**

In the previous article [10], we proposed an organic heterojunction theory based on the concept of quasiconductor. However, there were errors in the calculation. In the present article, we have corrected the derivation and revised the theory thoroughly.

The Modulus spectroscopy revealed that the carrier dynamics of OLEDs was quite different from that of the semiconductor diodes having a Schottky junction. It was shown that the roles of carriers in conductive and insulating states were switched in the organic devices and the semiconductor devices. The static behavior of carriers in organics as dielectrics has been overlooked. The polarization of each layer has a significant impact on the operation of multi-layered devices. We focus on the polarization dynamics of carrier accumulation and have shown that the carrier distribution is cleverly controlled through polarizations of the constituent layers. We derived a Mott-Schottky-equivalent equation by solving the Poisson equation and the continuity equation. Surprisingly, the equation can be approximated by the same capacitor equation derived in the previous article. Even though the quantitative
agreement is coincidental, there is a qualitative background that the polarization plays an essential role. The capacitor equation can describe not only the static carrier behavior of OLEDs but also the channel formation in OFETs. Organic multi-layered devices and semiconductor devices have intrinsic correspondences in the relations of conductor/insulator, insulating-depletion layer/conductive accumulation layer, and Mott-Schottky equation/capacitor equation as noted in the previous articles [10, 11]. The concept of quasiconductor was introduced to describe this duality for semiconductors. We consider that the quasiconductor is the missing link between organic electronics and semiconductors.
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Fig. 1. Carrier generation in quasiconductors. A neutral bound electron hole pair is generated by thermal excitation. The electron diffusion through the organic/metal interface generates a carrier. At high voltage, a direct injection from metal to organic or vice versa becomes the dominant one. (a) electron generation. (b) hole generation.
Fig. 2. Potential and charge distribution of a two-layer device with spontaneous polarization.

Blue thick lines are real charges and yellow thick lines are imaginary charges appearing at the edges of polarized layers. $\vec{P}_0$ is the spontaneous polarization in layer I and red broken lines are the polarization fields. Thick red lines are the internal potentials that are the sum of the polarization and the externally applied field. (a) the device is opened. (b) at the accumulation voltage where the externally applied electric field balances the spontaneous potential. (c) during the accumulation and decrease of the interface charges. (d) at the built-in potential.
Fig. 3. Potential and charge distribution of a two-layer device with fixed negative charges at the interface. I: ET layer, II: accumulated HT region, and III: non-accumulated HT region. Blue lines are real charges. $\sigma_s$ is the number of the fixed interface charges. (a) the accumulation voltage. (b) finite positive bias voltage. (c) the full accumulation voltage.