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Interfacial charges in organic hetero-layer light emitting diodes probed by capacitance–voltage measurements

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Abstract

The bias dependent capacitance of organic hetero-layer light emitting diodes (LEDs) based on *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphtyl)-1,1-biphenyl-4,4 diamine (NPB) and tris(8-hydroxyquinoline)aluminium (Alq_3) shows below the built-in voltage, a step-like change from a value corresponding to the total organic layer thickness to a higher value given by the Alq_3 layer thickness. The bias and frequency dependent behaviour of the capacitance can be explained by the presence of negative charges with a density of -6×10^{11} e/cm^2 at the NPB–Alq_3 interface. This leads to an inhomogeneous potential distribution inside the device with a discontinuity of the electric field at the organic–organic interface.

Keywords: Impedance spectroscopy; Organic light emitting devices; Interfaces

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1. Introduction

The measurement of the bias and frequency dependent capacitance is a well-established technique for the investigation of conductivity, doping and trap states in organic semiconductors. Here, we used this technique to obtain information on interfacial charges and the electric field distribution in hetero-layer devices comprising *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphtyl)-1,1-biphenyl-4,4 diamine (NPB) as hole transport material and tris(8-hydroxyquinoline)aluminium (Alq_3) as electron transport and emissive material. For this type of hetero-layer device, it has been found already from the analysis of current–voltage characteristics by Matsumura et al. [1] and from electro-absorption spectroscopy by Rohlfing et al. [2] that under forward bias the voltage drop at the Alq_3 layer is much larger than at the NPB layer. In the following, we will show that also under reverse bias condition, an inhomogeneous field distribution occurs which manifests itself in a voltage dependent capacitance. The origin of this quite unexpected behaviour is found in a negative interfacial charge density.

2. Experimental results

From current–voltage characteristics of NPB–Alq_3 hetero-layer devices, which have been studied by numerous authors, only very limited information about the physical processes in organic light emitting devices (OLEDs) can be obtained under reverse bias condition (here we will denote with reverse bias, a bias value below the built-in voltage given roughly by the contact potential difference of the electrodes; approximately 2 V for ITO and Ca). In contrast to the dc current, the complex impedance and especially the differential capacitance shows new features in reverse bias direction which will be discussed in the following.

Fig. 1 shows the capacitance of a series of two-layer devices with a 60 nm NPB layer and an Alq_3 layer with thickness ranging from 10 to 240 nm. In all cases, two different voltage regimes separated by a transition voltage V_T can be identified. For voltages well below V_T, the measured value of the capacitance is constant and is given by the overall thickness of the organic layers: $C_{tot}^{-1} = C_{NPB}^{-1} + C_{Alq_3}^{-1}$ as expected for two dielectrics in series. Above that value of V_T, the capacitance increases and reaches at the built-in voltage, a value equivalent to the capacitance of the Alq_3 layer alone: $C_{tot} = C_{Alq_3}$. Additionally, we found that the transition voltage V_T is independent of the NPB layer thickness [3]. However, from Fig. 1, it is evident that V_T decisively depends on the thickness of the Alq_3 layer. Obviously, the transition voltage is close to the built-in voltage for the thinnest Alq_3 layer and shifts towards zero and negative voltage with increasing Alq_3 thickness. The inset of Fig. 1 shows the dependence of the transition voltage V_T (taken as the inflection point of the C–V curves) on the Alq_3 thickness. Within the error limits given by the width of the transition and the thickness measurement, the

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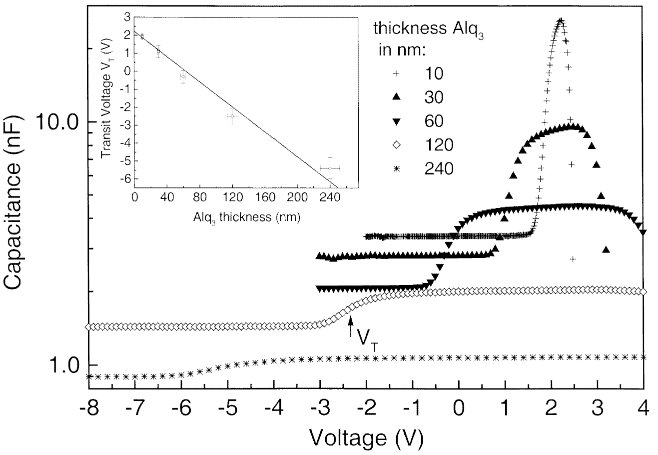

Fig. 1. Capacitance–voltage characteristics for a series of two-layer devices with a 60 nm NPB layer and varying Alq_3 layer thickness with ITO and Ca electrodes and a device area of 8 mm^2. The inset shows the dependence of the transition voltage on the Alq_3 thickness. The measurement frequency was 111 Hz.

transition voltage depends linearly on the Alq_3 thickness. The fitted straight line intersects the voltage axis at 2.2 ± 0.15 V, which is very close to the built-in voltage of 1.9–2.2 V estimated from current–voltage characteristics, and its slope is 0.35 ± 0.03 MV/cm.

Fig. 2a shows the frequency dependent capacitance for one thickness combination and two different bias values. When the bias is below the transition voltage ($V = -1$ V) at the given Alq_3 thickness, a frequency independent capacitance is found up to 300 kHz, where the influence of the leads becomes important, and the value of the capacitance is equal to the series sum of both capacitances. On the other hand, when the bias is between V_T and V_{bi} ($V = 1$ V), then below a relaxation frequency of about 50 kHz, the capacitance is equal to C_{Alq_3} before it drops again to the value $C_{tot}^{-1} = C_{NPB}^{-1} + C_{Alq_3}^{-1}$.

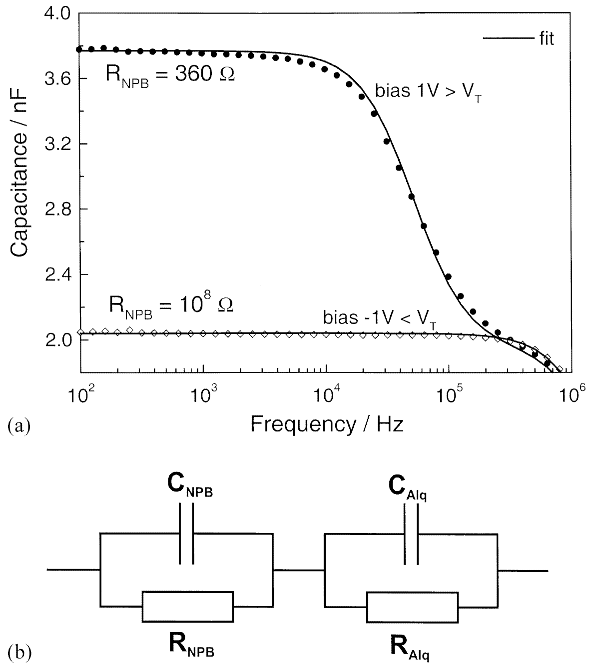

Fig. 2. (a) Frequency dependent capacitance for ITO/NPB (62 nm)/Alq_3 (55 nm)/Ca for a bias above (closed circles) and below (open square) the transition voltage. Also shown are fits (straight lines) to the equivalent circuit with $C_{NPB} = 4.2$ nF, $C_{Alq_3} = 3.8$ nF, $R_{Alq_3} = 10^8\ \Omega$ and R_{NPB} as indicated. (b) Equivalent circuit for the hetero-layer device in (a). The ITO series resistance of 35 Ω used in the fit has been omitted here for simplicity.

For an explanation of the above listed experimental observations, it is useful to consider the properties of the equivalent circuit of a hetero-layer device shown in Fig. 2b. Each organic layer is represented by a parallel circuit of a capacitor and a resistor connected in series. The lead resistance of the electrodes can be neglected for the discussion here. The values of the capacitance for each layer are determined by the geometry and the dielectric constant: $C_i = \varepsilon_i \varepsilon_r A / d_i$. The resistance values are given by the conductivity and the geometry: $R_i = \sigma_i d_i / A$. The important point is now that the resistance is a strongly bias dependent quantity, since the value of $\sigma_i = q n_i \mu_i$ changes when the carrier density n_i is increased by carrier injection. There are two limiting cases of interest here. One is that both the resistances, R_{NPB} and R_{Alq_3}, are very large such that at a given measurement frequency $\omega = 2\pi f$ the condition $\omega\tau_i \gg 1$ with $\tau_i = R_i C_i$ is fulfilled. Then the total capacitance of the circuit is just the series sum of the two individual capacitances: $C_{tot}^{-1} = C_{NPB}^{-1} + C_{Alq_3}^{-1}$. The second interesting limit is when one resistance, here R_{NPB}, is much smaller than the other and at the same time the measurement frequency is not too high such that $\omega\tau_{NPB} \leqslant 1$ holds. Then the measured total capacitance is just the Alq_3 capacitance: $C_{tot} = C_{Alq_3}$. In this case, the measured capacitance is frequency dependent showing a Debye relaxation process from the higher value $C_{tot} = C_{Alq_3}$ at low frequency to the lower value $C_{tot}^{-1} = C_{NPB}^{-1} + C_{Alq_3}^{-1}$ above the relaxation frequency $\omega_r = \tau_r^{-1}$ with $\tau_r = R_{NPB}(C_{NPB} + C_{Alq_3})$ [4]. Such a frequency dependence of the capacitance is indeed observed experimentally as shown for the two different bias values in Fig. 2a. From the relaxation frequency, the value of the NPB resistance at $V = 1$ V can be determined as 360 Ω which is orders of magnitude lower than for $V = -1$ V.

3. Discussion

The observation of two bias regimes with different overall capacitance can be explained by a drastic drop of the resistance of the NPB layer at the critical voltage V_T. This means that at the voltage $V_T < V_{bi}$, the NPB layer must have reached the flat band condition so that holes can be injected into NPB from the ITO anode. However, this in turn implies that at V_T, the applied voltage completely drops at the Alq_3 layer. Thus, the internal electric field in the NPB and Alq_3 layers is discontinuous at the interface between both materials. Following from Poisson's law such a discontinuity ΔF

of the electric field at an interface can only be caused by an interfacial charge density σ_0: $\Delta F = \sigma_0/\varepsilon_r\varepsilon_0$. At the transition voltage the flat band condition in NPB is reached implying that the voltage across the organic now drops completely over the Alq_3 layer. In this case, ΔF corresponds to the electric field in Alq_3 and thus the following relationship holds: $\sigma_0/\varepsilon_r\varepsilon_0 = \Delta F = F_{Alq_3} = (V_T - V_{bi})/d_{Alq_3}$. If the effect is a purely interfacial one, σ_0 should not depend on the Alq_3 thickness d_{Alq_3} and thus V_T should be a linear function of d_{Alq_3}. Indeed, the transition voltage shows such a linear dependence (inset of Fig. 1) indicating that the interfacial charge density does not depend on the thickness of Alq_3. The intercept of the straight line with the voltage axis at 2.2 ± 0.15 V corresponds well to the estimated built-in voltage of about 2 V as predicted by the above relation. From the slope, one directly obtains the magnitude of the interfacial charge density as $\sigma_0 = -6 \times 10^{11}$ e/cm^2. So, the physical reason behind the observed behaviour of the capacitance is the presence of negative interfacial charges at the NPB–Alq_3 interface under reverse bias. There may be additional dipole layers at the interfaces. However, this would not affect capacitance measurements — in contrast to photoelectron spectroscopy — because such dipole layers lead to discontinuity in the electrical potential but not in the electric field. Of course, such dipole layers would have an influence on the built-in potential which then is not simply given by the difference of the electrode work functions.

4. Summary

In organic hetero-layer light emitting diodes, an increased capacitance can be observed for reverse bias above a transition voltage V_T. This indicates that the NPB layer reaches the flat–band condition at V_T which is lower than the built-in voltage. To explain the increase of the capacitance negative interfacial charges must be assumed, the density of which can be derived from the thickness dependence of V_T to $\sigma_0 = -6 \times 10^{11}$ e/cm^2. A more formal treatment by Scheinert et al. [5] using numerical simulations shows that such a behaviour can be explained by charged acceptor-like trap states in the Alq_3 at the interface which are getting compensated gradually by injected holes when the bias exceeds the critical value V_T. The knowledge of such trap states is essential for a proper understanding of the physical processes at the organic–organic interface which in turn determines the efficiency of hetero-layer devices.

Acknowledgements

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