

Chemical Aging, Charge Transport, and Electroluminescence in Alq_3-based Organic Light-Emitting Diodes

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Abstract

Conduction in aluminum(III) 8-hydroxyquinoline (Alq_3) was modeled based on trap-charge limited conduction of electrons in the bulk. The evolution of a narrow Gaussian distribution of localized trap states below the lowest unoccupied molecular orbital (LUMO) of Alq_3, lying against a natural exponential background, was used to explain changes in the current-voltage characteristic and external quantum efficiency with time observed by many researchers for organic light-emitting diodes. Based on the change of the shape of the *J-V* curve, the depth of the electron trap states that were formed during aging was about 0.25 eV below the LUMO of Alq_3. An increase in drive voltage and decrease in efficiency is predicted with aging by this model for current densities in a reasonable range, assuming that the evolved trap states are non-emissive and also non-quenching. The products of chemical aging can account for the generation of traps at the observed depth.

Introduction

As organic light-emitting diodes (OLEDs) continue to gain a foothold in the display industry, it becomes increasingly critical to understand the long-term aging effects to keep device properties as constant as possible over their lifetimes. Operating at constant current density, OLEDs have a characteristic differential aging signature. The light output (or efficiency) of an OLED tends to fall while the drive voltage (or device resistance) increases; each process tends to occur more rapidly at short times. In aluminum(III) 8-hydroxyquinoline (Alq_3)-based OLEDs, the rates of these processes have been shown to increase at higher operational current densities.[1]

Chemical aging of Alq_3 has been reported,[2,3] but this has been difficult to observe in operational OLEDs, because for the mechanisms likely to produce failure (charge trapping or quenching), only minute concentrations of degradation products are required to see adverse effects in a device. The recent work of Aziz *et al.* shows evidence of luminescence quencher formation when Alq_3 is forced to transport holes,[4] and is probably the best evidence of chemical failure in active devices to date. This paper considers the earlier work of thermal degradation of Alq_3[5,6] and predicts the effects of this reaction on the *J-V* characteristics of an OLED fabricated from this material.

Experiment

The OLEDs in this study were deposited on indium tin oxide (ITO)-coated glass substrates, upon which was cast a 500 nm film of a doped hole transporting polymer in an effort to planarize the ITO surface.[7] These layers were spin cast at 1500 rpm from 25 mg/mL methylene chloride solutions of polymer and salt. The conduction in the polymer film was ohmic, with conductivity of about 10^{-6} to 10^{-5} S/cm. After the polymer deposition, the devices were constructed by thermal vacuum deposition of 50 nm of N,N'-bis-naphthyl-N,N'–bis-phenyl-4,4'-biphenyldiamine (NPB) to prevent quenching by the doped polymer, 50 nm Alq_3, 0.8–1.2 nm CsF, and 200 nm Mg or Al at a pressure of 1.5×10^{-6} Torr. *J-V* measurements were made with a HP 4155 semiconductor parameter analyzer, under a nitrogen blanket.

Model Development

Unipolar transport models have been used to describe the current density vs. voltage (*J-V*) characteristics of Alq_3-based OLEDs due to the significant mobility barrier for hole transport in Alq_3,[8] and the use of fluoride films produce low-resistance contacts for electron injection.[9-11] Of these single carrier models, those based on localized charge trapping in the bulk have been successful in fitting the typical power-law *J-V* characteristics of actual devices.[9,10] It is assumed for now that the current in these heterojunction devices is limited by conduction of electrons through the Alq_3 layer, perturbed slightly by the minority holes present near the interface. The electron-only assumption derives principally from the low hole mobility

of Alq_3 compared to the other layers. Transport of electrons is therefore limited by carrier trapping and the buildup of space charge in Alq_3 rather than by contact effects or mobility barriers in the hole transport layers. Preliminary experiments suggest that Alq_3/NPB blocking contact does not affect this characteristic, and recombination does not significantly affect the shape of the curve for devices of this type. These assumptions are plausible if hole transport to Alq_3 is efficient, and recombination is instantaneous and confined to the interface. Other issues with this model are discussed in more detail in another paper.[12]

Under such a representation, immobilization of carriers in bulk trap states limits the current at intermediate levels of charge injection. These states may arise from disorder,[13,14] lattice relaxation,[10] or impurities.[3,9,15] A transition to space charge limited (SCL) conduction, or trap-filled limit, may occur at high currents when all of the trap states are full and the strongest limitation on the electron transport is the space charge built up by free and trapped carriers.

The mathematical description of this system begins with the Poisson equation, which may be written as,[16]

$$\varepsilon\, dF/dz = e\,(n - n_0 + (n_t - n_{t0})) \qquad (1)$$

where F is the electric field in the z direction, and ε and e are the dielectric strength of Alq_3 and the elementary electron charge. The boundary condition $F(0) = 0$ was used, implying an infinite reservoir of electrons at the cathode, which for functionally ohmic contacts produces accurate solutions at distances adequately far into the device.[16] The free and trapped electron concentrations (n, n_t) are described by Fermi-Dirac statistics (the expressions for the equilibrium carrier concentrations are analogous). The trapped carrier concentrations are integrated over all energies within the band gap, E_G, expressed as,[16]

$$n_t = \int_{E_G}^{0} D(E)/(1+\exp(E-E_F/kT))dE \qquad (2)$$

$$\text{and, } n = Nc \exp(E_F/kT) \qquad (3)$$

(while taking the conduction band edge as zero). N_C is the effective density of states in the conduction band, E_F is the quasi-Fermi level (and is defined above), and E_G is measured optically at about 2.7 eV for Alq_3. The current flow equation, neglecting diffusion and for a single carrier, ($J = e\mu nF$ = constant) is used to explicitly state the electric field in terms of the free electron concentration, and the Poisson equation is then solved numerically.

The versatility of this formulation is that D(E), the density of trap states, can be described in any arbitrary fashion.[17] It is approximated as an exponential in this model, but as the energy states of individual moieties change their nature due to chemical aging, the shape of the distribution changes, and the J-V characteristic can be reevaluated accordingly.

The model employed is especially useful because it allows various distributions of trap states to be represented easily.[17] The density of states ($D(E)$ in Eqn. 2) is free to be any arbitrary distribution. An exponential distribution of trap states yields the power-law J-V relation used in the literature.[10,16] A discrete level lying against this exponential background, filled slowly, has been used to describe the gradual decay of injected hole current in anthracene crystals held at constant voltage.[18] We propose that a narrow Gaussian distribution of trap states can be used to approximate the presence of impurity species formed during the aging process. This is a good approximation of chemical aging, since a chemical impurity should have a well-defined unoccupied electronic state. The dissociation of Alq_3 in the presence of water to form 8-hydroxyquinoline (Hq) is a primary chemical degradation scheme,[3,19] and will be used to describe the aging for the remainder of this paper. The summed distribution of localized states (Gaussian plus exponential) is shown in Figure 2, and is expressed mathematically as,

$$D(E) = D1(E) + D2(E)$$
$$= (N_{t1}/E_{t1})\exp(E/E_{t1}) + (N_{t2}/E_{t2}')\exp(-(E-E_{t2})^2/E_{t2}'). \qquad (4)$$

$D1$ is the exponential background distribution of trap states, $D2$ is the new impurity distribution centered around E_{t2}, the trap depth. The other parameters E_{t1}, N_{t1}, E_{t2}', and N_{t2} further describe the shape of $D1$ and $D2$. E_{t1} describes the breadth of the exponential and is obtainable from the power-law portion of the J-V curve. Following Burrows *et al.*,[10] the density of states in the conduction band, N_C, was assumed to be about 1×10^{19} cm^{-3}, and N_{t1} was varied for a good fit.

Results and Discussion

The current density vs. voltage (J-V) characteristics of these devices are shown in Fig. 1. Three distinct regions are visible: (1) ohmic conduction ($J \propto V^1$) at low voltage; (2) a steep power-law ($J \propto V^{11}$) in the intermediate region; and (3) a square-law dependence ($J \propto V^2$) at high current densities. This behavior is predicted for unipolar charge transport in trap-filling insulators.[16] The transition to space charge limited (SCL) conduction, or trap-filled limit occurs at high currents when all of the trap states are full and the strongest limitation on the electron transport is the space charge built up by free and trapped carriers. This is and not others probably because holes do not penetrate far into the Alq_3 layer, as may occur when less resistive hole tranpsort layers are used.[12,20]

During chemical reaction, a state in the conduction band or localized tail of Alq_3 (*i.e.*, an Alq_3 ligand) is converted to 8-hydroxyquinoline, which has a LUMO at a lower energy. (The remaining ligands associated with aluminum are assumed to be approximately isoenergetic with those on Alq_3, and no selectivity between Alq_3 and partially reacted species is considered at this time.) For an arbitrarily narrow ($E_{t2}' = 0.05$) trap distribution, Equations 1-4 were solved numerically, including a built-in potential of 1.05 V, a reasonable value for the work function difference between magnesium and plasma-treated ITO.[20] The corresponding J-V curves for conversion to -0.3 eV and -0.5 eV traps are shown in Figure 2. The changes in the

curves reflect the total density of states evolved: conversion = $\int_E D2dE / N_c$. The values shown in the figure depend therefore on the original density of states proposed for the LUMO, and are somewhat arbitrary. It can be clearly seen that the presence of trap states at these levels causes a pronounced increase in the resistance of the OLED even at low conversions, qualitatively explaining the device decay characteristics which are observed in experiment.

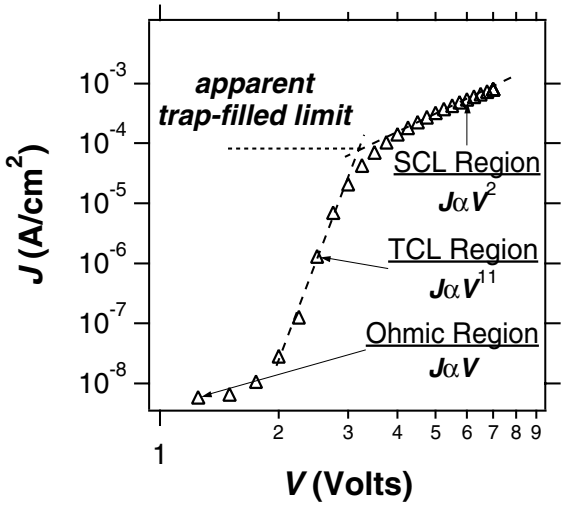

Figure 1. J-V characteristics of the devices showing three regions of conduction. (1) ohmic conduction at low currents, (2) a $J \propto V^{11}$ law at moderate levels, and (3) $J \propto V^2$ behavior at high currents.

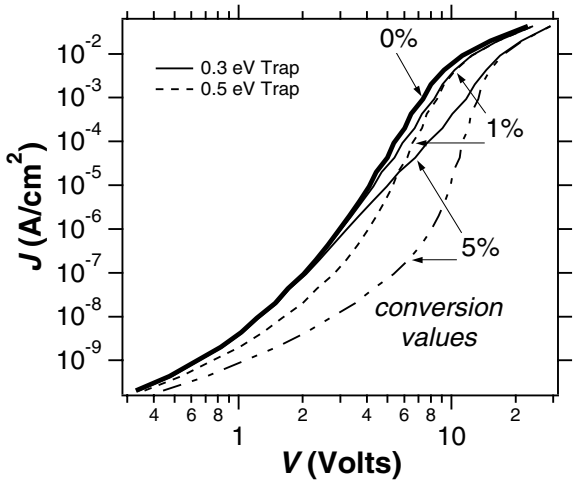

Figure 2 Simulated J-V characteristics as a function of aging in an Alq_3-based OLED.. The dark solid line is a simulated curve for zero conversion. The thinner solid lines are for 1% and 5% conversion to trap states 0.3 eV below the LUMO of Alq_3; dashed lines are 0.5 eV below. Inset is the modeled distribution of localized states below the LUMO, consisting of a background exponential and a Gaussian peak whose relative area varies with conversion.

The shape of the *J-V* curve changes as a function of the trap distribution. Shown in Fig. 3 are *J-V* curves taken at various times from an OLED stressed at 150 μA/cm^2. At low current densities, the curves are identical within experimental error. They begin to deviate from the original at approximately 3 V and then converge asymptotically to the same V^2 (SCL) law at higher bias. Based on the simulations presented above, this point of deviation corresponds to an impurity trap level slightly less than 0.25 eV below the conduction band of Alq_3. This is consistent with characterization of the LUMO of Hq relative to Alq_3 as measured by cyclic voltammetry (taking into account the precision to which the values are known),[21] as well as independent measurements placing the trap depth between 0.25 and 0.13 eV.[22]

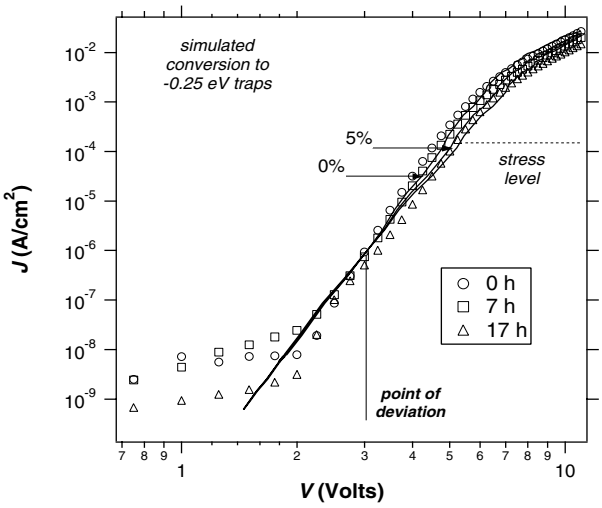

Figure 3. J-V characteristics taken at various times for a device stressed at 150 μA/cm^2. Successive curves begin to deviate from the original at about 3 V and then reconverge to the same square-law behavior at higher bias. This corresponds qualitatively to the simulations where traps are generated -0.25 eV below the Alq_3 LUMO, shown by the solid curves.

There remain several important factors to be considered with respect to this model. Current efforts are underway to represent the bipolar nature of the devices and blocking character of the junction, and experimental work goes toward verifying some of the assumptions listed earlier. Charge transport through the localized states by hopping is also currently ignored, even though it can predict a power-law dependence in the absence of well-defined traps.[9] Thermal effects are expected to be quite significant, and are not considered by this model, limiting it as a predictive tool especially at higher currents. Also, not all species are considered for the aging reaction. For example, Hq is not a stable electron trap, and goes on to form species which both quench the luminescence and act as deeper electron traps when reduced in the presence of air.[21] Thus far, the only transient considered is the chemical aging; charging

transients in polyethylene films and organic crystals have been known to persist hours to months,[13,18] although the small thickness of the Alq_3 films should minimize these effects. The success of AC drive schemes, however,[1] suggests that charging transients may still be important, and the chemical instability of charge-trapped species may partially account for this.

Conclusion

Despite several caveats, a simple unipolar charge transport model was used to fit the *J-V* characteristics of Alq_3-based OLEDs. This model was very useful in predicting the effect of chemical aging processes in these devices. The data reveal a characteristic trap depth of about 0.25 eV below the LUMO level of Alq_3, which is consistent with the measurement of Alq_3's degradation products and with independently measured trap states in Alq_3.[3,22]

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Biography

Dr. Papadimitrakopoulos received his Ph.D. from University of Massachusetts, Amherst in 1993. He worked as a postdoctoral fellow at Bell Laboratories from 1992 to 1994. In 1994, he joined the University of Connecticut faculty, where he now holds the position of associate professor. He is a co-founder of the Nanomaterials Optoelectronics Laboratory, which pursues research in organic light-emitting diodes, supramolecular self-assembled structures, and polymer-quantum dot composites.