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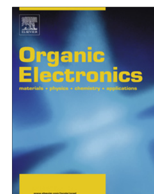

Analysis of electron traps formed in organic films with a sputtered cathode

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ABSTRACT

To understand why performance degradation is reduced for sputtered cathodes on organic devices when the electron transport layer (ETL) is doped with Li, we analyze electron-only devices using the thermally stimulated current (TSC) technique and modeling of temperature-dependent current–voltage characteristics with a trapped-charge-limited current (TCLC) model. The combined results suggest that the trap density measured by TSC might also include a portion of the density of the hopping sites in the lowest unoccupied molecular orbital levels, which contributes to charge transport. Compared to undoped devices, doped devices maintain a high density of hopping sites even when the Al is sputtered. We propose that the reduced effect of sputtering on electron injection and transport properties is because radical anions of Alq_3 might still be formed by the strong reducer Li even if the organic material is partially damaged. An additional TSC peak and increased driving voltage for doped tris(8-hydroxyquinoline)aluminum (Alq_3) as an ETL with a sputtered cathode suggests the formation of new traps possibly because of damage even though the transport is better compared to the undoped device. Such traps are not found in doped bathophenanthroline (Bphen) as an ETL, which shows no change in driving voltage.

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1. Introduction

In recent years, the considerable development of organic light-emitting diodes (OLEDs) has led to their application in various commercial displays such as smartphones and large-screen TVs, and great effort has been put into developing flexible displays and large-area lighting devices continuously [1–3]. To realize the mass production of OLEDs, large-area substrates and high-throughput manufacturing are required. One process challenge that must be solved to achieve mass production is the deposition of the final metal electrode, which is often an aluminum cathode. While conventional evaporation has been widely used to deposit cathodes such as Al for OLEDs, evaporation boats made of W or BN and crucibles made of SiC or AlN usually corrode during Al deposition [4–6], making them unreliable. Since high temperatures are needed to evaporate Al, heating of the substrate and splash from the boat to the substrate are also issues. Thus, alternatives to evaporation are desired for mass production.

Sputtering has been well established for the mass production of liquid-crystal displays and has numerous advantages over conventional evaporation such as compatibility with large-area substrates, high throughput, and the ability to deposit alloys and oxide semiconductors

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[7,8]. However, high-energy particles such as Ar^{+} ions, electrons, and Al neutral atoms and UV light from the plasma often seriously damage the devices when the cathode is directly sputtered onto organic layers. The sputter damage usually results in an increase of driving voltage and a decrease of luminance efficiency in OLEDs [9,10]. Thus, methods to minimize the reduction in performance when using sputtering are desired.

In a previous report, we demonstrated that sputtering could be used to fabricate the cathodes without degrading performance by introducing an electron transport layer (ETL) doped with 1% Li [11]. The driving voltages at 50 mA/cm^2 were almost identical for OLEDs using Li-doped bathophenanthroline (Bphen) with the thicknesses of at least 40 nm as an ETL regardless of whether the cathode was sputter or evaporation deposited. Furthermore, similar operational lifetime could be obtained by doping the ETL regardless of the electrode deposition method. In contrast, a slight increase of driving voltage of 2.5 V was observed when Li-doped tris(8-hydroxyquinoline)aluminum (Alq_3) was used as the ETL. Although performance could be maintained by using sputtering in tandem with a doped ETL layer, the mechanism of the performance changes with and without the Li-doped ETL is still not clear.

The purpose of this paper is to characterize the damage caused by sputtering in ETLs to better understand the origin of the change in performance when switching between evaporation and sputtering. Because damage caused by sputtering is expected to lead to carrier traps in the organic layers, we focus on two methods to characterize traps in organic films: the thermally-stimulated current (TSC) technique and the analysis of the temperature dependence of current density vs. voltage (J–V) curves using a trapped-charge-limited current (TCLC) model. We compare the properties measured by the two methods for electron-only devices (EODs) and study the effect of doping and cathode deposition on both the density of states in the lowest unoccupied molecular orbital (LUMO) band and the properties of the charge traps.

2. Theory

In this study, we use two different methods to evaluate carrier traps in the organic devices. The first method of TSC has been widely used to analyze carrier traps in inorganic semiconductors [12,13], evaluate carrier traps in organic materials [14–17], and investigate degradation in OLEDs [18,19]. In TSC, carriers are first frozen into the traps by flowing current through the device at low temperatures to fill the traps. The trapped carriers are then released by slowly increasing the temperature, and information regarding the number and depth of traps can be obtained based on the current flow through the device under a constant forward bias at each temperature. Assuming that all trapped electrons released during the temperature sweep are collected by the electrodes and that they all contributed to TSC, the total electron trap density $\left(N_t^{TSC}\right)$ can be calculated using [19],

$$N_t^{TSC} = \frac{Q}{qAL} \tag{1}$$

where Q is the total charge, which is equal to the area under the TSC peak, q is the electronic charge, A is the active device area, and L is the cathode–anode spacing.

Further information regarding the trap density, depth, and distribution can be gained by using multiple cycles called thermal cleaning [20–22]. After filling the traps at low temperature (T_{start}), the device is heated to a temperature T_{stop} while measuring the current. When T_{stop} is reach, the device is again cooled to T_{start}, and the device is then heated to a new, higher T_{stop}. This process is repeated for multiple cycles. By measuring multiple cycles in this manner, the peaks and trap densities for each trap level can be better separated.

During thermal cleaning, the TSC current (I_{TSC}) with a constant heating rate under the condition of slow retrapping can be expressed as [23]

$$I_{TSC} \cong I_0 \exp\left(-\frac{E_t^{TSC}}{kT}\right). \tag{2}$$

Here, I_0 is the total trapped current, E_t^{TSC} is the trap depth measured by TSC, k is Boltzmann's constant, and T is the temperature. Using Eq. (2), the trap depths E_t^{TSC} for each cycle can be calculated from the slope of the Arrhenius plot of I_{TSC} on the low-temperature side of the peak of the TSC maximum. Here, we follow the initial rise method [22,23], in which only the low current range of the initial rise portion of the TSC (up to 20% of the TSC maximum) is used for fitting Eq. (2) [23].

Secondly, we modeled the temperature dependence of the J–V characteristics as TCLC to separately obtain information on the depth and density of traps and the density of states in the LUMO band [24–26,17]. At high voltages, sufficient carrier injection occurs in organic thin films and all of the traps are filled, and the current is expected to be space-charge limited and increase as the square of the voltage. However, the traps will not be completely filled at lower voltages. As the traps begin to fill, the effective mobility will increase because of the lowering chance for trapping of the injected carriers. In this regime, the current follows a power-law dependence higher than the square of the voltage.

Previous studies have shown that the TCLC can be modeled by assuming an exponential distribution of trap energies [27] in the band gap with the density of traps per unit energy centered on the energy E having the form [25]

$$N_t^E(E) = \left(\frac{N_t^{TCLC}}{kT_t^{TCLC}}\right) \exp\left(\frac{E - E_{LUMO}}{kT_t^{TCLC}}\right). \tag{3}$$

Here, N_t^{TCLC} is the total trap density, T_t^{TCLC} is the characteristic temperature of the exponential trap distribution, E_{LUMO} is the LUMO energy level, and the characteristic trap energy is defined as $E_t^{TCLC} = kT_t^{TCLC}$. In this case, the current density in the TCLC regime J_{TCLC} can be described by [25]

$$J_{TCLC} = N_{LUMO}\mu_n q^{(1-m)} \left(\frac{\varepsilon m}{N_t^{TCL}(m+1)}\right)^m \left(\frac{2m+1}{m+1}\right)^{(m+1)} \times \frac{V^{(m+1)}}{d^{(2m+1)}}, \tag{4}$$

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