Interface injection-limited carrier-transport properties of Alq3

A. UDDIN 1, a, C.B. LEE 1, X. HU 1, T.K.S. WONG 2

1 School of Materials Engineering, Nanyang Technological University, 639 798 Singapore
2 School of Electrical and Electronic Engineering, Nanyang Technological University, 639 798 Singapore

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ABSTRACT We have studied the carrier-transport properties of the amorphous organic material tris (8-hydroxyquinoline) aluminium (Alq3) for Al and LiF/Al cathodes at room temperature. The investigation was made by the current–voltage characteristic measurements for different Alq3 film thicknesses. It is found that the current–voltage characteristic has a linear dependence on the thickness of the Alq3 film. The current density increases by several orders for a LiF/Al cathode over that of Al at a given bias voltage. The carrier-injection processes at the metal/organic contact dominate the current–voltage characteristics. The carrier injection seems to be limited by the charge hopping of interfacial molecular sites.

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1 Introduction

Organic semiconductors, especially molecular organic thin films, have recently received much attention for their potential applications in a wide variety of optoelectronic devices [1, 2]. Despite the technological success in this area, many of the electronic transport properties of organic devices still remain unknown.

The organic molecular material tris (8-hydroxyquinoline) aluminium (Alq3) is one of the most promising candidates for optoelectronic devices due to its adjustable high absorption and electrical behaviour, which are comparable to crystalline inorganic semiconductors in many respects. The electrical properties of organic semiconductors are much less defined and controlled compared to crystalline semiconductors. Usually, the electrical properties of organic thin films are strongly sample-dependent due to the presence of unintentional impurities and defects [3].

Charge transport in organic semiconductors is characterised by the localisation of electronic states to individual molecules and disorder in the positions and the energy levels of those molecules. As a result, charge transport occurs via thermally activated hops with a mobility that typically increases with both electric field and temperature [2, 4]. The broad density of states at the interface and the narrower bulk distribution are qualitatively similar to trapped charge limited models. The interfacial model requires energetic disorder in the bulk and dipole-induced disorder at the interface to explain these distributions. In the case of bulk materials, an injection model should explain the thickness dependences of current–voltage characteristics over many orders of magnitude and it should also explain the variations in injection for different cathode materials [5].

For the cathode–organic interface, enhanced electron injection is desired in order to balance charge carriers in the active layer. The most commonly used low work function electrode metals are Mg, Cu, Li, Al, Au, etc. [6, 7]. All of these materials are highly reactive after exposure to moisture and oxygen and they comprise fast-diffusing species. Among them Al is a much more desired cathode material as it is relatively stable and resistant to oxidation. However, Al has a higher work function as a cathode with an organic layer compared to other metals. The improvement in Al performance as a cathode is achieved by the use of a thin interlayer at the Al/organic interface. This layer could be formed by depositing a thin layer of LiF or other alkali-metal insulators, by doping the near-interface region of Alq3 through co-evaporation with Li or by doping the near-interface region of the Al cathode with LiF [8]. The effect of LiF in improving device efficiency is still not fully understood. There are several mechanisms proposed for the enhanced electron injection, such as electron tunnelling through a thin insulating layer, band bending at the metal/organic interface, lowering of the work function of Al, the presence of interfacial dipoles and LiF dissociation with released Li atoms reacting with Alq3 to form Alq–anions [8, 9], although there seems to be a wide belief of LiF dissociation as the dominant mechanism.

In these studies we have used cathodes of Al and LiF/Al on an amorphous organic semiconductor Alq3 to study the transport properties of carriers. It is observed that a broad dipole-induced Gaussian distribution of sites at the interface creates sufficient energetic disorder to dominate the transport characteristics. To gain a more fundamental understanding of charge injection at metal/organic interfaces, one must derive the energetic distribution of interface states. One must also understand the chemistry at the interface, as well as the physical origins of interface dipoles that lead to the lowering of the...
interface energy barrier and determine the width of the interfacial state distribution.

2 Experimental

We have prepared thin-film electron-injection amorphous Alq₃ devices for different thicknesses with two electrodes Al and LiF/Al on glass substrates. The device structure used in all measurements consists of two electron-injecting cathodes Al and LiF/Al, a variable-thickness layer of Alq₃ and a 0.1-µm-thick ITO anode to inject holes. The layers were deposited by a thermal evaporator under high vacuum (10⁻⁶ Torr). To prevent oxide formation on the anode, there was no vacuum break between its deposition and the deposition of the Alq₃ layer. Cathodes consisted of either a 1000-Å-thick layer of Al or a 10-Å LiF layer followed by a 1000-Å Al layer. Each cathode size was controlled by metal deposition through a shadow mask with 2-mm-diameter holes.

Glass substrates were pre-cleaned in a bath of deionized water and detergent and subjected to ultrasonic vibrations to remove dust and other microscopic particles, before being rinsed in sequential applications of deionized water, acetone, boiling trichloroethylene, acetone and isopropanol. The measurements were performed in air, but samples were stored and saved under nitrogen atmosphere to minimize the oxidation of the cathode.

3 Experimental results and discussion

The current-density ($J$)–voltage ($V$) characteristics were measured for both electrode (Al and LiF/Al) samples by a HP 4145B semiconductor parameter analyser at room temperature. The measured $J$–$V$ curves for Al and LiF/Al electrodes are shown in Fig. 1 for the 1000-Å-thick Alq₃ layer in both the samples. Two distinct regions can be seen in the log $J$–log $V$ characteristics plotted: a low applied bias region with a small slope and a high applied bias region with a much larger slope. Some devices also showed a further change to a smaller slope at much higher applied bias, indicating that a third region is present, which is not shown in the graph. The first region is below about 2 V, the current then rising rapidly with applied bias in the second region. At temperatures below 210 K this transition region is reported to have disappeared [10]. In terms of space charge limited (SCL) conduction, the different regions in the $J$–$V$ characteristics would be explained in terms of either a change in the field dependence of the mobility and/or the movement of the Fermi level through different trap distributions in the carrier energy gap [5, 11].

The main difference between the Al and LiF/Al electrodes is that, for a given thickness of Alq₃, the LiF/Al cathode devices have a current density several times higher than that of the Al cathode devices at a given bias voltage $V$. This may not be due to the addition of the small negative carrier current from electron injection, but rather due to its compensating effect on the large SCL positive carrier current [11]. Therefore, although it is reasonable to assume that the Al devices are dominated by the majority positive carrier current, this can only be treated as a first approximation and a more detailed study would have to take into account the small minority negative carrier current and the effect of the small amount of carrier recombination.

It is believed that the carrier-injection efficiencies of the cathodes decrease with increasing cathode metal work functions. But the observed slopes of the log $J$–log $V$ characteristics are nearly independent of the work function, in contrast to the predictions of thermionic emission theory [12]. Moreover, the carrier-injection efficiency of these cathodes at a constant electric field should be exponentially dependent on the magnitude of the injection barrier. There are two possible explanations for these discrepancies: firstly, there may be intermediate states participating in the injection process, so that injection does not occur in a single hop and, secondly, interface interfacial dipoles at the contact may significantly alter the effective injection barrier for each cathode material [10]. The presence of interfacial dipoles may also induce the intermediate states that participate in the injection process. Hopping out of a Gaussian distribution of intermediate states within the organic material near the metal injection interface yields current–voltage characteristics that closely approximate a power-law behaviour [5]. In addition, the organic material may possess extrinsic trap states due to impurities or damage introduced in the film-deposition process and cathode metal diffusion into the organic material [13, 14].

These extrinsic states influence charge transfer, perhaps explaining variations in the injection-limited current–voltage characteristics observed with different samples of Alq₃. But, irrespective of possible extrinsic effects, variations in the local dipole strength and orientation must result from randomness in the interface morphology and the localisation of charge in molecular materials. Disorder in the local interfacial dipole field significantly broadens the energy distribution of organic transport states in the interfacial layer, such that the initial hop from the metal Fermi level is not the most energetically costly injection event. One can assume that charges from the metal are readily injected into a broad distribution of interfacial states from which they must hop into a narrower, higher-energy distribution of transport states. Although transport is dominated in this case by the effects of disorder, electric field screening by the metal contact also reduces the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) splitting energy at the interface by

![FIGURE 1 Current density in Alq₃ with applied bias voltages for Al and LiF/Al cathodes at room temperature. The thickness of the Alq₃ film was 1000 Å for both samples. The current density for a LiF/Al cathode is much higher than the Al cathode for the same bias voltage](image-url)