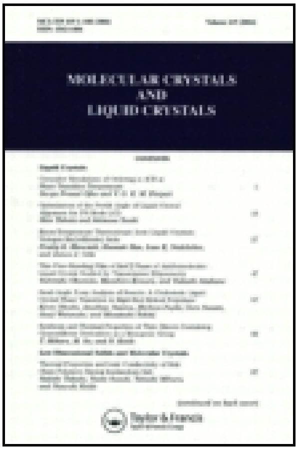

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Current Characteristics of Pristine and Tetrathianaphthacene-Doped Tris(8-Hydroxyquinoline) Aluminum (ALQ_3) Thin Films

Suidong Wang [a] , Kaname Kanai [b] , Eiji Kawabe [b] , Yukio Ouchi [b] & Kazuhiko Seki [c]

[a] Research Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

[b] Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

[c] Research Center for Materials Science and Institute for Advanced Research, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

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Suidong Wang
Research Center for Materials Science, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya, Japan

Kaname Kanai
Eiji Kawabe
Yukio Ouchi
Department of Chemistry, Graduate School of Science,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

Kazuhiko Seki
Research Center for Materials Science and Institute for Advanced
Research, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

We report our study on the current-voltage characteristics of single layer devices employing pure and heavily tetrathianaphthacene (TTN)-doped tris(8-hydroxyquinoline) aluminum (Alq_3) films as active layers. Sandwich structures with magnesium (Mg) top and bottom electrodes were employed in the devices. In the undoped device, the current increases exponentially with the applied voltage, and is concluded to be limited by the carrier injection at the Mg/Alq_3 interface with a small injection barrier. With the same device structure, both the bulk-doped and interface-doped devices show a bulk-limited current flow, which is much larger than that in the undoped device and behaves as trap-free space-charge-limited current (SCLC) with a field-independent mobility. The improvement of the current is ascribed to the large enhancement of carrier injection by the doping. An increase of the magnitude of the interfacial dipole has been proposed as the possible cause for the enhancement of carrier injection.

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Address correspondence to Kazuhiko Seki, Research Center for Materials Science and Institute for Advanced Research, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8602, Japan. E-mail: seki@mat.chem.nagoya-u.ac.jp

Keywords: Alq_3; carrier injection; current-voltage characteristics; doping; organic light emitting diodes

INTRODUCTION

Organic light emitting diodes (OLEDs) have progressed at a rapid rate in the past years. Carrier injection and carrier transport are key issues in the devices, and studies on them are important both in the fundamental understanding and in improving the device performance. Current-voltage (J-V) characteristics of organic-based devices with diode structures [1–3], and with metal/organic/metal structures have been investigated [4–11]. It is recognized that injection-limited current and bulk-limited current dominate in the devices when the energy barriers to carrier injection are large enough and negligible, respectively.

To improve the device efficiency, good contacts which facilitate carrier injection are highly desirable. Intentional molecular doping is one of the techniques to lower the operating voltage of OLEDs [12]. Large increase of current density in hole transport organic materials was achieved by p-type doping [13,14]. Increase of bulk conductivity of organic material by n-type doping was also reported [15], but successful electrical molecular doping in tris(8-hydroxy-quinoline) aluminum (Alq_3), the most widely used electron transport material in OLEDs, is still absent. We demonstrate our recent study on the J-V characteristics of the single-layer devices with pristine and heavily tetrathianaphthacene (TTN)-doped Alq_3 films sandwiched between two magnesium (Mg) electrodes.

EXPERIMENTAL

Alq_3 with high purity was provided by Nippon Steel Chemical Co., Ltd.; TTN was synthesized after literature [16], and was carefully purified with gradient sublimation. Their chemical structures are inserted in the figures. The devices were fabricated on glass substrates in a high vacuum system, where the base pressure is about 5×10^{-7} Torr and the thickness of the deposited films was monitored with a quartz crystal microbalance. The doped films were grown by co-sublimation, and the dopant concentration ($\sim 10\%$) was controlled by the ratio of the deposition rates. All the devices have the same structure of 100-nm-Mg/300-nm-Organic/50-nm-Mg/Glass; the organic layer in the interface-doped device is composed of 10-nm-doped-Alq_3/280-nm-Alq_3/10-nm-doped-Alq_3. *In situ* measurements were performed at room temperature in the same chamber just after the fabrication. Since holes can not be efficiently injected into Alq_3 from Mg due to a high injection

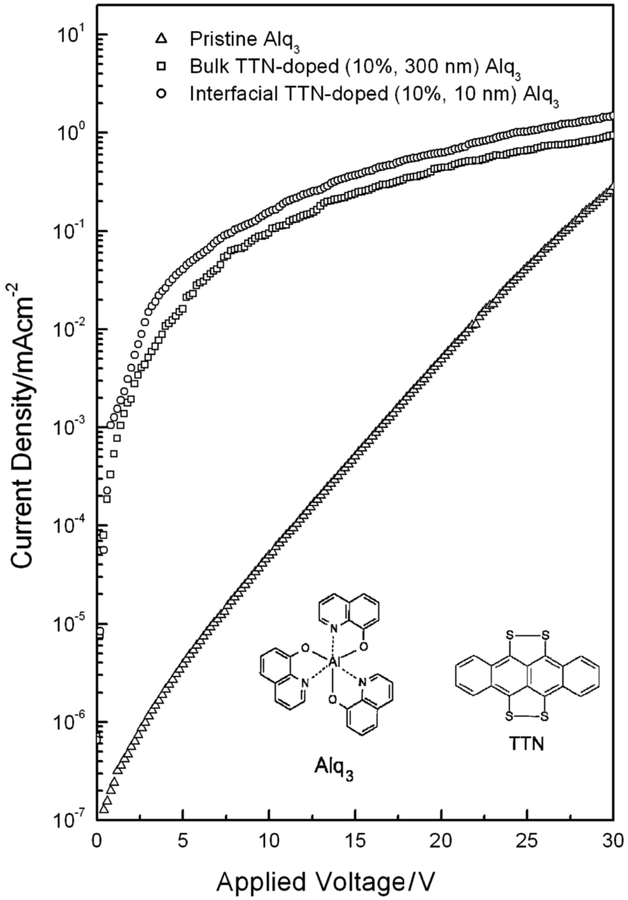

FIGURE 1 *J-V* characteristics of Mg/(TTN-doped) Alq_3/Mg devices. In the devices electrons are injected from the bottom contacts.

barrier [8], and there was no light emission observed even at high electric fields, the devices can be regarded as electron-only devices.

RESULTS AND DISCUSSION

The *J-V* characteristics of the devices are depicted in Figure 1. Note that only the forward characteristics corresponding to electron injection from the bottom contacts are shown in Figure 1, which are almost identical with the reverse characteristics (not shown). The identity is consistent with the previous studies on the metal/Alq_3/metal structures [7,8], indicating the deposition sequence has little influence on the carrier injection properties of the interfaces. The current density of the undoped device (triangle) is very small at low electric fields and increases exponentially with the applied voltage. A similarity of the current behavior was observed in the bulk-doped (square) and the interface-doped (circle) devices. The current density at relatively low electric fields is several orders of magnitude larger than that of the undoped device, while the logarithm of the current density is sublinear with the applied voltage.

For carrier injection from metals into dielectrics over a Schottky barrier, the *J*-*V* characteristics is usually described by the Richardson-Schottky (RS) thermionic emission model, i.e. $J \sim \exp(F^{1/2})$, where *F* is the electric field [17]. Figure 2 shows lg*J*-$F^{1/2}$ plots of the

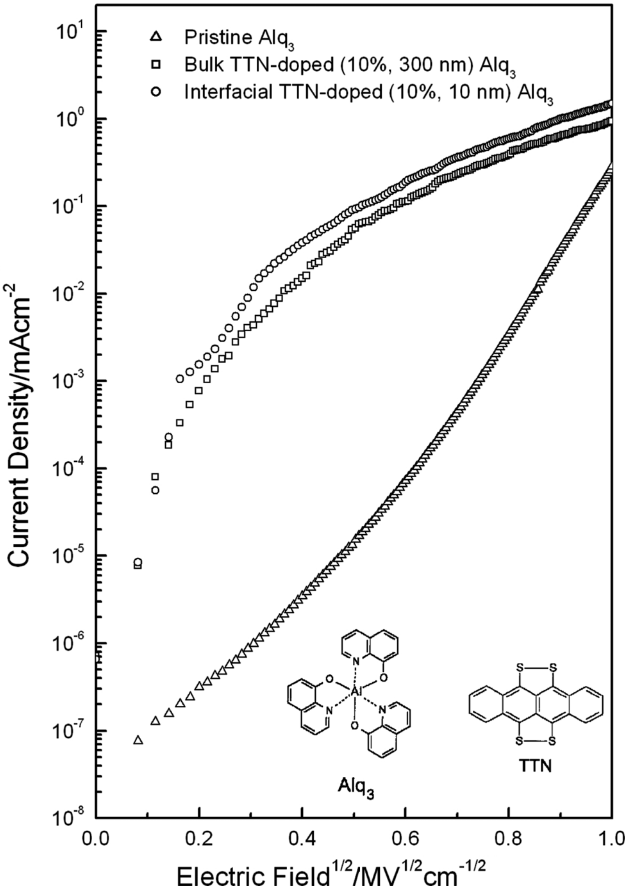

FIGURE 2 lg*J* versus $F^{1/2}$ plots of the data shown in Figure 1.

devices data. For the undoped device, lg$J$ yields a closely linear dependence on $F^{1/2}$, which accords with the prediction of the RS model. The small variance from the linear relationship at low electric fields may be induced by the leakage current. Moreover, the slope of the fitted straight line is 0.0083 (cm/V)$^{1/2}$, close to the RS model-derived value of 0.0076 (cm/V)$^{1/2}$. Still, however, we should note that the RS model was developed for high mobility materials in which the electronic states are highly delocalized. Thus theoretically it is not fully applicable to the present amorphous Alq$_3$ films. Barth and coworkers have shown the resemblance of field dependence but the quantitative differences to the RS model in their Alq$_3$-based devices [6]. Taking account of the charge recombination rate at metal/organic interface, Scott and Malliaras have proposed an analytical expression for the net injection current [18]

$$J = 4qN_0\mu F\psi^2 \exp(-\phi_B/kT)\exp(q\sqrt{qF/4\pi\varepsilon\varepsilon_0}/kT) \tag{1}$$

where N_0 is the density of chargeable sites in the organic film, μ is the charge carrier mobility, ϕ_B is the zero-field barrier height, and ψ is a function of the reduced electric field [18]. We tested the undoped device data by lg($J/F\psi^2$)-$F^{1/2}$ plots (not shown), and observed a closely linear relationship similar with that of lg$J$-$F^{1/2}$ plots in Figure 2. Furthermore, assuming $N_0 \approx 10^{22}\,\mathrm{cm}^{-3}$ and $\mu \approx 1 \times 10^{-6}\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$, based on the present experimental data (the ordinate intercepts of lg($J/F\psi^2$)-$F^{1/2}$ and lg$J$-$F^{1/2}$ plots), the barrier heights Φ_B derived from Eq. (1) and from the RS model are 0.26 eV and 0.63 eV, respectively. The comparison indicates that the injection current over a small barrier of 0.26 eV into a disorder organic film may be equivalent to that over a large barrier of 0.63 eV into a band-type material. Therefore, we conclude that the current in the undoped device is injection-limited even though the injection barrier is only 0.26 eV, as a consequence of the amorphous nature of Alq$_3$. Under the assumption of a common vacuum level, the barrier height for electron injection in present case is determined by the energy difference between the lowest unoccupied molecular orbital (LUMO) of Alq$_3$ and the Fermi level of Mg, which is about 0.7 eV. However, considerable vacuum level offsets normally with a negative value relative to the metal side were observed at most metal/organic interfaces, and the offsets will modify carrier injection barriers [19]. Kahn's group observed a dipole barrier of approximate 0.5 eV pointing down from Mg into Alq$_3$ by photoemission spectroscopy [8], the offset implies the electron injection barrier at the Mg/Alq$_3$ interface is only about 0.2 eV, in agreement with the present deduced value.

For contacts where carriers can be readily injected into an organic film, the field gradient caused by the high concentration of the injected carriers would limit the current density. If the effects of trapping and field dependence of mobility are neglected, the space-charge-limited current (SCLC) follows the Mott-Gurney square law [20]

$$J = \frac{9\varepsilon\varepsilon_0\mu V^2}{8d^3} \tag{2}$$

where d is the thickness of the organic film. J-V^2 plots of the devices data are shown in Figure 3. An explicit linear dependence of J on V^2 in both the bulk- and interface-doped devices is observed, implying a trap-free and field-independent SCL conduction. The similarity

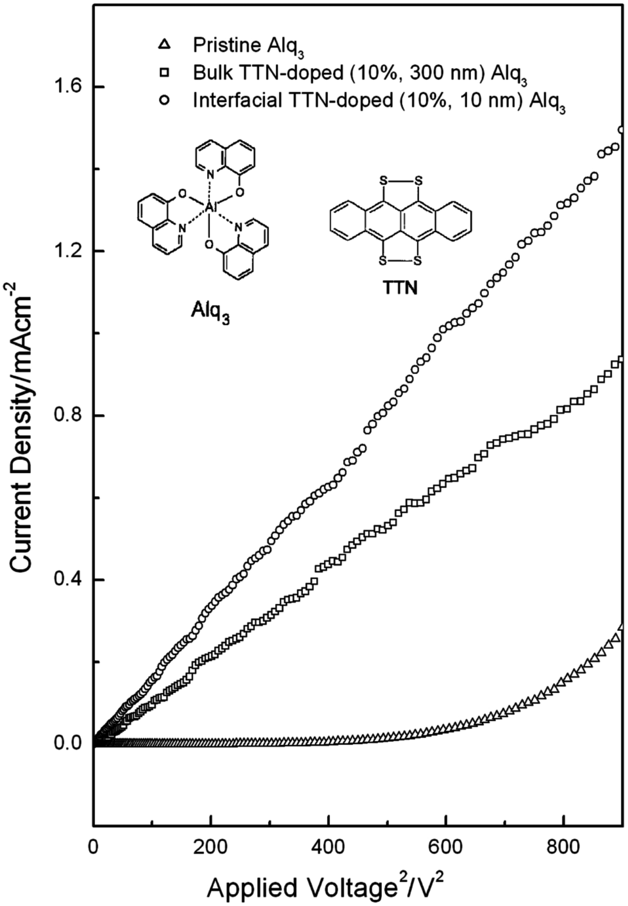

FIGURE 3 J versus V^2 plots of the data shown in Figure 1.

between the bulk- and interface-doped systems excludes the possibility of electric conduction through TTN, even if there is diffusion of TTN. The slightly larger current density in the interface-doped device might be due to that, the electron mobility is a little higher in pure Alq_3 compared with that in the doped films. The results indicate the current become bulk-limited by either the bulk-doping or the interface-doping, resulting from the strong enhancement of electron injection.

From the results above, we believe that the interesting phenomenon arises from the modification of the interfacial electronic structure. Since the reported energy of the highest occupied molecular orbital (HOMO) of TTN (4.2 eV) is 1.2 eV below that of the LUMO of Alq_3 (3.0 eV) [19], it is not easy to expect a high efficiency of charge transfer between the molecules. Thus the mechanism for TTN-doped Alq_3 may be different from the formation of a narrow depletion layer in the doping systems with energy matching [13,14], although we still point out that the coulombic stabilization of the $TTN^{\partial+}$-$Alq_3{}^{\partial-}$ pair, which occurs instantaneously during the charge transfer process, can reduce the charge transfer barrier to some extent. As another possible mechanism to explain the doping effect, we mention that the heavy doping of TTN may modify the interface and results in an increase of the interfacial dipole, for example, from 0.5 eV at Mg/Alq_3 to 0.7 eV at Mg/TTN-doped Alq_3. If this occurs, the electron injection barrier will decrease accordingly from about 0.2 eV to nearly 0 eV, and the removal of the barrier will enhance the electron injection from Mg into the LUMO of Alq_3. A change of the interfacial dipole by 0.3 eV was actually reported in the system of zinc phthalocyanine (ZnPc) on gold by the heavy doping of tetrafluorotetracyanoquinodimethane (F_4-TCNQ) [13].

CONCLUSION

The large improvement of the current characteristic of the Alq_3-based single layer device was achieved by the TTN heavy doping. The device based on pure Alq_3 exhibits the J-V characteristics approximately with a field dependence of $\lg J \sim F^{1/2}$, the current in which is injection-limited. In contrast, trap-free constant-mobility SCLC behavior ($J \sim V^2$) was observed in the TTN-doped devices (both bulk-doped and interface-doped), indicating that the current is bulk-limited due to the facile carrier injection. The modification of the interfacial dipole has been proposed as a possible cause for the enhancement of electron injection. The observed effect is expected to have potential applications in the organic-based devices.

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