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Deep-Level Characterization of Tris(8-Hydroxyquinoline) Aluminum with and without Quinacridone Doping

Yoshitaka Nakano, Koji Noda, Hisayoshi Fujikawa, Takeshi Morikawa, and Takeshi Ohwaki

Toyota Central Research and Development Laboratories, Inc.

Nagakute, Aichi 480-1192, Japan

Phone: +81-561-63-4302 Fax: +81-561-63-5328 E-mail: y-nakano@mosk.tytlabs.co.jp

1. Introduction

Tris(8-hydroxyquinoline) aluminum (Alq_3) has been widely used as the emitting layer and/or the electron-transporting layer for organic light-emitting diodes (OLEDs) based on small molecules. However, there is still a lack of understanding concerning the nature of carrier transport in this material. So far, the optical and electrical properties of Alq_3 have been studied in detail by using various physical and electrical techniques, but the fundamental electronic properties have still not been well understood.

Deep-level optical spectroscopy (DLOS) is well known as a powerful tool for the characterization of electronic deep levels in the band gap of semiconductors. This technique measures changes in the depletion region capacitance under optical excitation and can provide detailed mapping of the deep levels that would be undetectable by thermal emission techniques such as deep-level transient spectroscopy (DLTS) and thermally stimulated currents (TSC). In this study, we have first applied DLOS measurements to the Alq_3 -based devices and have investigated deep levels in order to provide more direct information on electronic trap states in the Alq_3 and quinacridone-doped Alq_3 ($\text{Alq}_3\text{:Qa}$) layers from the viewpoint of carrier dynamics.

2. Experimental

The $\text{Alq}_3/\text{LiF}/\text{Al}$ and $\text{Alq}_3\text{:Qa}/\text{LiF}/\text{Al}$ device samples were fabricated on indium-tin-oxide (ITO, $10\Omega/\square$, 150nm thick) coated glass substrate. The Alq_3 and $\text{Alq}_3\text{:Qa}$ layers (100nm) was respectively thermally evaporated, and then an Al layer (150nm) with an ultra-thin LiF (0.5nm) was formed as top contacts. Here, the Qa doping concentration in the $\text{Alq}_3\text{:Qa}$ layer was 1%. The Al electrodes had a square of 2.5mm. The LiF layer was used to reduce the barrier height for electron injection into the Alq_3 and/or $\text{Alq}_3\text{:Qa}$ layers from the Al electrodes. Finally, metallic In was deposited directly onto the top surface of the ITO layer to provide an ohmic electrode.

The capacitance-voltage (C-V) and conductance-voltage (G-V) measurements were performed at room temperature at 1kHz and a voltage step of 0.1V with a

delay time of 30s. DLOS measurements were conducted at room temperature at 1kHz by measuring the photocapacitance transients as a function of optical excitation energy, starting from 0.78eV up to 4.0eV [1]. The device samples were illuminated from the backside with monochromatic light. The photocapacitance transients were recorded for 300s after the onset of the illumination. The samples were maintained under zero-bias conditions. Prior to optical excitation, the deep levels were filled with electrons in the dark by applying a forward pulsed voltage of 5V, followed by a 5s delay in order to minimize any possible thermal transient contributions to the photocapacitance.

3. Results and Discussion

Figure 1 shows typical room-temperature C-V and G-V curves at 1kHz for the $\text{ITO}/\text{Alq}_3/\text{LiF}/\text{Al}$ and $\text{ITO}/\text{Alq}_3\text{:Qa}/\text{LiF}/\text{Al}$ device samples. Similar tendencies are seen for both samples. In forward bias, the capacitance exhibits a small shoulder at around -3V and the conductance increases significantly as the bias voltage is increased further. In particular, this capacitance behavior represents charging and discharging of electronic trap states in the Alq_3 and $\text{Alq}_3\text{:Qa}$ layers as follows. The small increase in capacitance due to the charging of the traps is observed under small forward bias from 0 to -3V, while the decrease in capacitance, due to the neutralization of the traps with significant electron and hole injection, is seen under a large forward bias. In this double-carrier injection process, numerous holes seem to be directly injected into the trap states from the conduction band of the ITO electrode, considering mismatched band alignment between the Alq_3 and the ITO layers.

Figures 2 and 3 respectively show typical room-temperature DLOS spectra at 1kHz of the $\text{ITO}/\text{Alq}_3/\text{LiF}/\text{Al}$ and $\text{ITO}/\text{Alq}_3\text{:Qa}/\text{LiF}/\text{Al}$ device samples. Here, the filling pulse widths were chosen as 10, 100, and 1000ms in order to evaluate carrier-injection rate dependence of trap states in the Alq_3 and $\text{Alq}_3\text{:Qa}$ layers. As shown in Fig.2, we can observe a midgap state emission at ~1.39eV (known as D), in addition to near-band-edge (NBE) transitions at 2.2-3.6eV for the Alq_3 sample. The

NBE feature is attributable to the HOMO band of the Alq₃ layer. Additionally, this NBE feature depends strongly on the double-carrier injection rate into the Alq₃ layer; the effective band gap (E_1) of the Alq₃ layer becomes narrow from 3.05 to 2.80 eV with increasing the carrier injection rate. This band gap narrowing is probably associated with variation in structural configurations of the Alq₃ layer by charging and discharging of the trap states. More importantly, the D level is a discrete deep level with an optical threshold at ~ 0.92 eV, independent of the carrier injection rate. In addition, the D level is found to interplay strongly between the LUMO and the HOMO bands, that is, the D level can be active as an efficient generation-recombination (GR) center that may impact the photophysical properties. Furthermore, carrier transitions from the D level show opposite behavior, due to the band gap narrowing by the carrier injection as stated above. From filling pulsed voltage dependence of DLOS spectra, the D level is considered to be an intrinsic nature of the Alq₃ layer, rather than newly introduced by degradation caused by hole injection [1,2]. Furthermore, given that the D level is located in the middle of the band gap, this GR center is probably attributable to an electrically neutral dangling bond state in the Alq₃ layer. On the other hand, as shown in Fig.3, the Alq₃:Qa layer shows a small emission peak at ~ 2.40 eV (known as E_2) and an energetic blue shift of the D level with increasing the carrier injection rate, compared to the Alq₃ layer. Considering that the E_2 level newly shows up in the spectra by the Qa doping, this level probably corresponds to the HOMO band of the Qa dopant. In addition, the observed blue shift of the D level indicates a strong interaction of the D level with the E_2 level characteristic of the Qa. In other words, the D level is subject to charge up positively due to the presence of holes injected into the E_2 level for the Alq₃:Qa layer, which is significantly different from the situation of the Alq₃ layer.

4. Conclusion

We have investigated band gap states in Alq₃ and Alq₃:Qa on fabricated ITO/Alq₃(:Qa)/LiF/Al devices by using a DLOS technique. DLOS measurements after double-carrier injection into the Alq₃ layer revealed a discrete trap level located at ~ 1.39 eV below the LUMO band. The pronounced 1.39 eV level is attributable to an intrinsic nature of Alq₃ and can be active as an efficient GR center that may impact the photophysical properties. Additionally, this GR center is subject to charge up positively due to the presence of holes injected into the E_2 level newly formed by the Qa doping for Alq₃:Qa.

References

- [1] Y. Nakano et al., *Appl.Phys.Lett.* **88**, 252104 (2006).
- [2] H. Aziz et al., *Science* **283**, 1900 (1999).

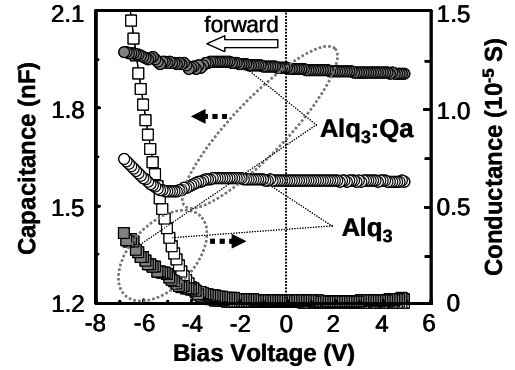


Fig. 1 Room-temperature C - V and G - V curves at 1 kHz for the ITO/Alq/LiF/Al and ITO/Alq₃:Qa/LiF/Al devices.

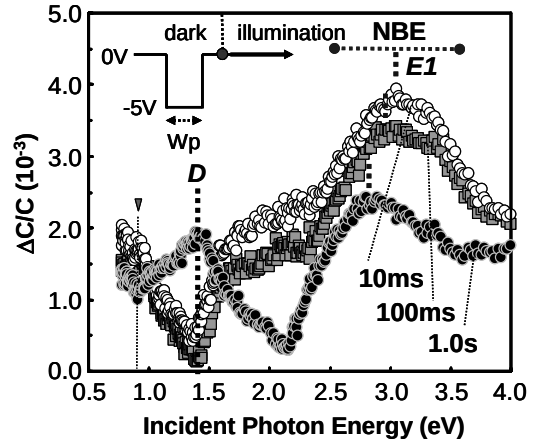


Fig.2 Filling pulse width dependence of room-temperature DLOS spectra at 1 kHz of the ITO/Alq₃/LiF/Al device.

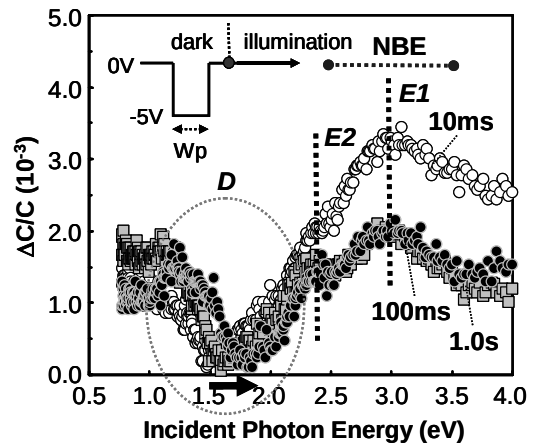


Fig.3 Filling pulse width dependence of room-temperature DLOS spectra at 1 kHz of the ITO/Alq₃:Qa/LiF/Al device.