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## Electroluminescence Enhanced from Electrode Interface in ITO/Tetracene/Al Diodes

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*We investigated emission spectra of ITO/tetracene/Al diodes for fully understanding carrier behavior in the device. By applying an A.C. square voltage, we showed that two distinct peaks were enhanced at around 545 nm and 615 nm. The peak at 545 nm is ascribed to intrinsic carrier process leading to bulk-originated EL, whereas the peak at 615 nm is due to interfacial carrier process via carrier traps nearby the electrodes, resulting in OLED degradation. To discriminate interface- and bulk-originated EL, A.C. frequency dependence of the EL spectrum was analyzed with taking into account carrier transit and carrier injection.*

**Keywords** Bulk-originated EL; electroluminescence; interface- and bulk-originated EL

### Introduction

Recently organic devices such as organic light emitting diodes (OLEDs) and organic field effect transistors (OFETs) have been intensively studied. In 1965, Helfrich *et al.* reported the observation of electroluminescence (EL) from the anthracene single crystal sandwiched between liquid and liquid electrodes [1]. This was the first to show the EL emitted from organic low-molecular weight materials. Since then EL has been a fundamental research subject of organic materials, and EL has drawn much attention in electronics [2] as well as in electrical insulation engineering [3]. The report by Tang *et al.*, regarding the possible high efficient EL radiation from a double-layer diode with Alq<sub>3</sub> and diamine [4], has given greatly an impact to scientific community, and organic EL is now available in display devices and lighting sources. However for the practical application of EL devices, fundamental studies

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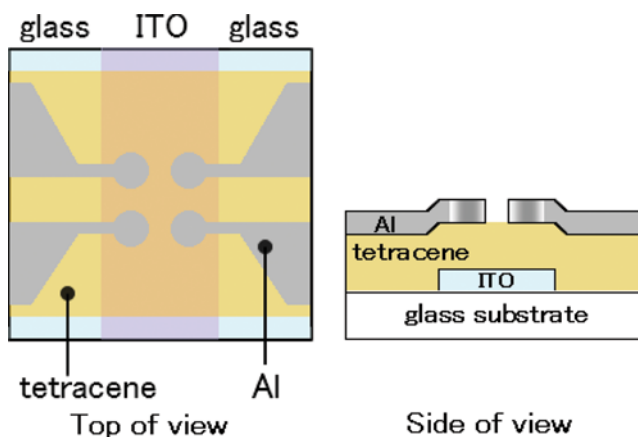
regarding device degradation are of great importance. This motivated us to study EL radiation from organic EL devices in terms of degradation.

We observed the EL spectrum from tetracene FETs by applying an A.C. square voltage, and found two distinct peaks, one is due to intrinsic carrier process leading to bulk-originated EL, and the other is due to interfacial carrier process via carrier traps [5]. Since the latter one is radiated from the edge of the source and drain electrodes at a wavelength longer than the main peak, this EL presumably related with the degradation of the EL devices. In this study, we demonstrate the similar longer-wavelength emission from general sandwiched-type single layer OLED in terms of device degradation. Spectrum measurement of EL from ITO/tetracene/Al diodes was performed under applying A.C. square voltage, and we observed the additional EL spectrum peak at a longer-wavelength region of the intrinsic peak at a wavelength of 545 nm.

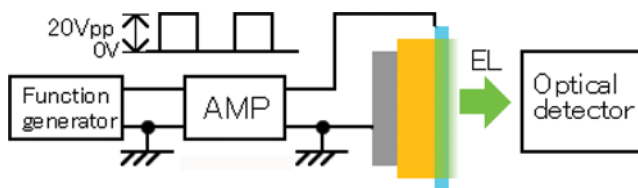
## Experiments

The devices used in the experiment were MIM [ITO/tetracene/aluminum (Al)] diodes (see Fig. 1). Tetracene, which was purchased from Sigma-Aldrich, was deposited on a pre-cleaned ITO substrate by resistive thermal evaporation. During tetracene evaporation, the process pressure was maintained below  $2 \times 10^{-6}$  Torr. Then Al electrode was deposited on tetracene film to fabricate the MIM structure. The process pressure during metal evaporation was approximately  $1 \times 10^{-5}$  Torr. Thickness of tetracene and Al layer was 400 nm and 100 nm, respectively, controlled using a quartz crystal microbalance (QCM). Diameter of circular shaped electrode was 1 mm. All devices were encapsulated using small vial with silica-gel and deoxidizer to avoid the degradation due to the humidity and oxygen.

Figure 2 shows the experimental setup used for the EL measurement. The EL device was driven by applying A.C. square voltage supplied from a function generator with a high speed amplifier. Amplitude of the applied voltage was 20 V. For the luminescence spectrum measurement, multi-channel spectroscope (B&W Tek, BTC112E) was used as an optical detector. On the other hand, photo multiplier tube



**Figure 1.** Top and side view of sample structure for ITO/tetracene/Al diode.

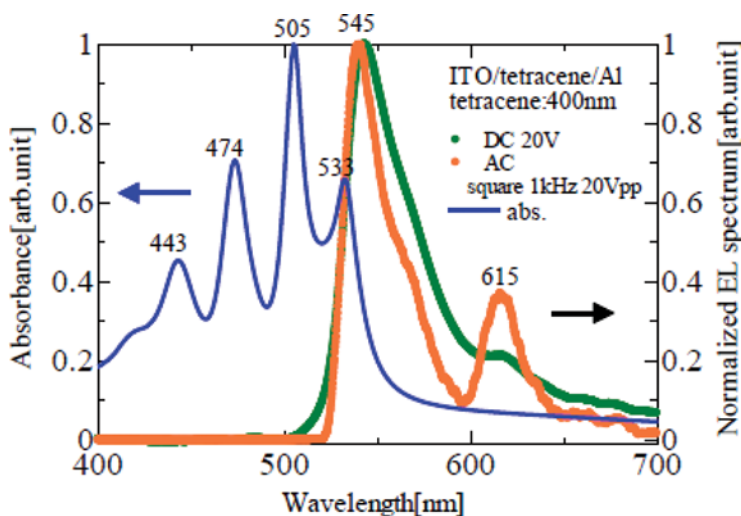


**Figure 2.** Experimental setup for the EL measurement.

(PMT: Hamamatsu, R3896) was used for the intensity measurement at fixed wavelength. Interference filter was used to separate the specific wavelength (540 and 610 nm) to distinguish the intrinsic and surface originated luminescence. All measurements were carried out in dark.

## Results and Discussion

Figure 3 represents the EL spectra of ITO/tetracene/Al diodes measured under applying D.C. and A.C. square voltage, indicated together with the absorption spectrum. As shown in the figure, an apparent peak was observed at around 545 nm in the EL spectra under D.C. voltage application. The absorption spectrum suggests that this peak is attributable to the transition from the first excited singlet state to the ground state [7]. It should be noted that energy gap between the HOMO and LUMO level of tetracene is 2.4 eV [6], and a wavelength of 545 nm corresponds to 2.3 eV. Further, the peak position of the EL under D.C. application is almost coincident with that of photo-luminescent (PL) peak. These imply that the origin of the peak at 545 nm is assigned to the intrinsic process originated from tetracene molecules. Besides the main peak at 545 nm, an additional peak was clearly observed at around 615 nm under A.C. square voltage application. Different spectra observed



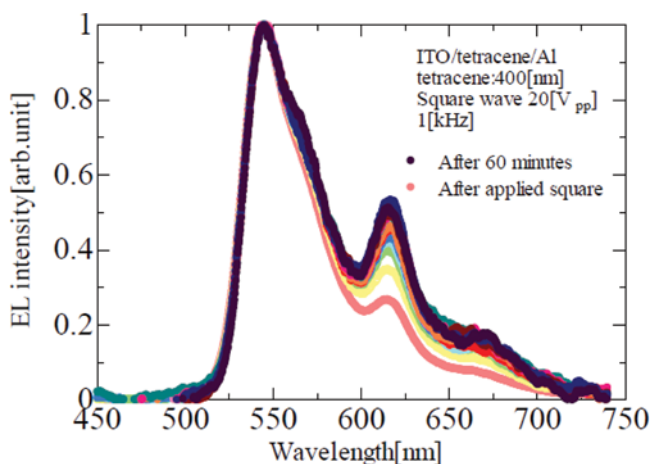
**Figure 3.** The absorption spectrum of tetracene, the EL spectra of ITO/tetracene/Al diodes measured under D.C. and A.C. square voltage.

under A.C. and D.C. application indicate the corresponding different EL mechanisms work in the device under A.C. and D.C. voltage application.

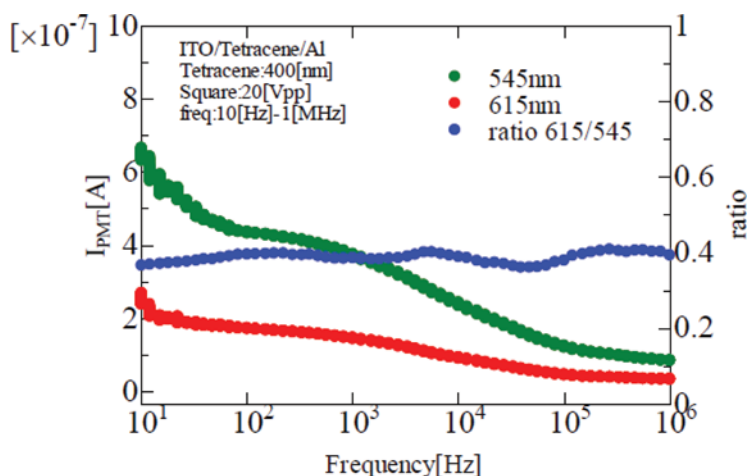
Figure 4 shows the spectrum change of EL emission with the elapsed time. All spectra are normalized to the peak intensity of the intrinsic emission at 545 nm. Interestingly, spectral intensity at 615 nm gradually increases with the elapsed time. Increase of the relative intensity at a wavelength of 615 nm is reasonably attributed to the degradation of the device. Degradation proceeds under the device operation, and the electrode interface is more easily damaged in comparison with the bulk region in the EL device. According to the thermally stimulated current (TSC) measurements [8], the depth of hole traps in tetracene was estimated about 0.34 eV. This trap depth is almost coincident with the energy difference between 545 nm and 615 nm in wavelength, i.e., 0.39 eV. Thus, the interfacial degradation increases trap sites leading to the increase of the emission at 615 nm.

Holes and electrons are continuously injected from ITO and Al electrode under the D.C. voltage application, and the recombination takes place in the bulk region of the tetracene film. Thus, intrinsic recombination process dominates under the D.C. voltage application leading to 545 nm emission. On the contrary, under the A.C. square voltage application, carriers are injected alternating (see Fig. 2 for applied pulse sequence). In such situation, recombination region should be dependent on an A.C. frequency. For a lower frequency, recombination dominantly takes place in a bulk region of the tetracene layer, whereas recombination region is confined at an interfacial region nearby the electrode for higher frequency operation. It can be easily understood on the basis of carrier transit time. Carriers injected from one electrode are conveyed by the electric field and reach to the opposite electrode, if the transit time of carrier is shorter than the half period of the A.C. square voltage.

Transit time of the device is given by  $t_{tr} = d^2/\mu V$ , where  $d$  is a film thickness.  $\mu$  and  $V$  represent the carrier mobility and applied voltage, respectively. Carrier mobility is obtained from a slope of the I-V characteristics in the SCLC region as  $\mu \approx Id^3/\epsilon_r\epsilon_0SV^2$ , where  $\epsilon_r$  is dielectric constant. For the samples used here, the carrier mobility is calculate as  $1.3 \times 10^{-8} \text{ cm}^2/\text{Vs}$ , and the transit time of  $t_{tr}$  as  $12 \times 10^{-3} \text{ s}$ . The calculated values support the intrinsic EL emission in the region of frequency



**Figure 4.** The spectrum change of EL emission with the elapsed time.



**Figure 5.** The frequency dependence of the intensity ratio between 545 nm and 615 nm emission.

lower than around 100 Hz, owing to the electron-hole recombination. On the other hand, the EL emission in the frequency region higher than around 100 Hz is ascribed to the EL, mainly caused by the interfacial carrier process assisted by alternating electron-hole injection.

Figure 5 shows the frequency dependence of the intensity ratio between 545 nm and 615 nm emission ( $I_{615}/I_{545}$ ). The ratio was nearly constant over the entire region. The increase of the ratio around the transit time should be observed if the degradation is dominant. Nevertheless we could not see such behaviors in Figure 5, though the results clearly showed the EL emission at 545 nm in higher frequency region. To understand the degradation mechanism and modeling the degradation process, we need to further study carrier injection process, trapping process, carrier transit process, carrier distribution process, carrier recombination process, etc. Now further measurements of the frequency dependence are proceeding to reveal the origin of a longer-wavelength emission from ITO/tetracene/Al diodes. Finally we should note that the EL process via interfacial states in MIM devices is possible in a way similar to the OFET device. This is one of our findings in the preset study.

## Conclusion

Emission spectra of ITO/tetracene/Al diodes were investigated to understand carrier behavior in the device. By applying an A.C. square voltage to the diodes, we showed that two distinct peaks were enhanced at around 545 nm and 615 nm. The peak at 545 nm is ascribed to intrinsic carrier process leading to bulk-originated EL, whereas the peak at 615 nm is due to interfacial carrier process via carrier traps nearby electrodes, resulting in OLED degradation.

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