Direct probing of charge carrier behavior in multilayered organic light-emitting diode devices by time-resolved electric-field-induced sum-frequency generation spectroscopy

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Organic light-emitting diodes (OLEDs) have attracted significant attention as next-generation full-color display devices, and are beginning to be widely used in mobile phones and OLED television sets. OLEDs also exhibit potential for providing energy savings in a range of applications, including lighting and flexible panel displays. Indeed, since the development of high-efficiency double-layer OLEDs, the emission efficiency and device reliability of OLEDs have greatly improved. In the context of their structure, current highly efficient OLEDs have a characteristic multilayered structure, where each organic layer has a different function. More specifically, the interfacial structures and properties of the OLEDs in relation to charge separation, transfer, and accumulation at the interfaces and ultrathin organic layers are of extreme importance in determining their charge carrier behavior, as both the charge transport and the concentrations of charge carriers in organic thin-film layers are directly associated with the functions of multilayer OLEDs. Furthermore, the formation and decay of electronically excited states, in addition to the generation and recombination of carriers within the organic layers and interfaces, are essential processes in OLEDs. Therefore, examination of the carrier dynamics in multilayer OLEDs under operation is of particular importance. The time-of-flight method is one of the useful techniques of probing carrier motion in organic materials, but it is difficult to apply this technique to real multilayer devices. Transient electroluminescent measurements are also helpful for exploring carrier behaviors, however, it cannot provide information on carrier behavior until the electroluminescence is generated. Although investigation of the charges present in such organic devices can be performed by transient electroluminescence, it cannot provide information on carrier behavior; therefore concluded that time-resolved EFI-SFG is useful for directly probing the carrier behavior in OLEDs in addition to identifying the origin of the charge carriers present in OLEDs. © 2017 The Japan Society of Applied Physics
CN (60 nm)/α-NPD (20 nm)/6 wt% Ir(ppy)3/CBP (30 nm)/
BAlq (10 nm)/Alq3 (30 nm)/LiF (1.6 nm)/Al (150 nm). All
devices were prepared on a transparent CaF2 substrate
to give an emission area of 2 × 2 mm2. A sealed glass cap
containing a desiccant protected the organic layers from
the permeation of ambient moisture.

The basic SFG system employed herein was described in
our previous paper.15) All reported SFG spectra were obtained
using a PPP polarization combination, in which infrared (IR),
visible, and SFG light were polarized in the plane of incidence,
and the incident angles of the visible and IR beams were 70 and
50° from the surface normal, respectively. The prepared multi-
layer OLEDs were operated with the application of a pulse
square wave voltage using a pulse delay generator (Stanford
Research Systems DG535) and a high-speed bipolar ampli-
sifier (NF HSA4101). Emission from the OLEDs was detected using
a photomultiplier (Hamamatsu H10721) equipped with a high-
speed preamplifier (Hamamatsu C9999), and was stored by
an oscilloscope (Tektronix TDS-2022C). The injected current
was monitored using a current probe (Tektronix TCP2020) and
again stored by an oscilloscope.

The emission response of the OLEDs and the EFI-SFG
intensity response at 1600 cm−1 under application of the square-
wave bias voltage of 10 V are shown in Fig. 1(b), where
the pulse width is set to 15 μs. In addition, the SFG signal
intensity at 1600 cm−1 according to the applied square-wave
bias voltage is shown in Fig. 1(c). As indicated, emission from
the OLEDs begins following a charge injection of ∼1 μs.
Furthermore, as shown in Fig. 1(c), the SFG signal intensity
varies upon the application of a pulse voltage to the OLEDs.

The time-resolved EFI-SFG spectra of the OLEDs taken at
the visible excitation wavelength of 460 nm are shown in
Fig. 2. Prior to application of the voltage, the obtained SFG
spectrum was comparable to the previously reported SFG
spectrum of the OLED device in the absence of a bias
voltage.14) As indicated, the SFG curves display signals at
1386, 1400, 1442, 1459, 1485, 1504, 1516, 1550, 1586, and
1606 cm−1, the majority of which are derived from the vibra-
tional modes of Alq3.14,33) Upon the subsequent application of a
pulsed bias voltage to the OLEDs, the intensities of the Alq3
SFG peaks at 1386, 1442, 1504, 1572, 1590, and 1605 cm−1
were immediately reduced. In addition, after 150 ns, the peaks
at 1497, 1557, 1567, and 1600 cm−1 began to increase in intensity
until 1 μs, after which time few variations in peak intensity
were observed. Moreover, as indicated in Fig. 1(b), emission
from the OLEDs began after this time (i.e., >1 μs). We
previously reported that the increase in SFG peak intensity
upon the application of a bias voltage was due to the electric-
field-induced effect caused by charge accumulation in the α-
NPD layer.14,17) In contrast, upon removal of the pulse voltage,
the peak at 1567 cm−1 disappeared within 200 ns, although the
signal at 1600 cm−1 corresponding to α-NPD remained. It is
therefore apparent that the peak at 1567 cm−1 does not orig-
inate from the neutral α-NPD molecules. In addition, under
these conditions, the intensities of the SFG peaks derived from
Alq3 began to increase, as shown in Fig. 2(b). Approximately
1 μs after the removal of the pulse voltage, the SFG spectrum
essentially returned to its previous unbiased shape.

To confirm the origin of the SFG peak at 1567 cm−1, the
SFG spectra of both the 3-nm-thick α-NPD film deposited on
the 3 nm MoO3 layer and of the 3 nm MoO3 thin film
deposited on the 5 nm α-NPD layer were recorded at the
visible excitation wavelength of 460 nm [Fig. 3(a)]. In both
cases, as MoO3 is a strong electron-accepting material, α-NPD
cations were formed upon oxidation by MoO3,33) thereby
resulting in an intense signal at 1570 cm−1. In addition, a
shoulder was also observed at 1600 cm−1 in both spectra,
which was attributed to the neutral α-NPD species. We note
that the observation of the strong SFG peak from the α-NPD
cations must be due to the doubly resonant effect. Recent
Raman studies suggest that the optical absorption spectrum
of α-NPD cations has a broad peak centered at 492 nm, and
the resonant Raman can be observed even by excitation at
532 nm.18) It therefore appears that the TR-EFI-SFG peak
observed at 1567 cm−1 originates from the cationic α-NPD
species. It should also be noted that no signals corresponding
to MoO3 were observed in this region [see Fig. 3(a)]. In
addition, the SFG spectrum of the α-NPD thin layer deposited
on HAT-CN exhibited only a single peak at 1600 cm−1, with
no signal corresponding to the cationic α-NPD species being
observed. This clearly indicates that the α-NPD cations are not
formed by the simple deposition of α-NPD on HAT-CN.
Furthermore, the peak at 1567 cm−1 appears only following
the application of the bias voltage to the OLEDs, disappearing again upon its removal. This observation suggests that the α-NPD cations are generated at the HAT-CN/α-NPD interface upon the application of a forward bias voltage. The rapid disappearance of the cation peak immediately after removing the bias voltage indicates that the α-NPD cation disappears upon charge recombination at the HAT-CN/α-NPD interface. This finding was further confirmed by the examination of the SFG spectra of the α-NPD hole-only device (HOD) at various bias voltages [Fig. 3(b)]. In this case, the HOD structure was composed of the following: IZO (110 nm)/MoO_3 (10 nm)/α-NPD (150 nm)/MoO_3 (10 nm)/Al (100 nm). As indicated, upon the application of the forward bias to the α-NPD HOD, positive charges are injected into the HOD. Although the SFG peak shape of the α-NPD cations is slightly different from the chemically oxidized α-NPD cations, as shown in Fig. 3(b), the SFG peak intensity at 1570 cm\(^{-1}\) increases significantly upon application of the forward bias voltage, indicating that the α-NPD cations are formed when positive charges are injected into the α-NPD layer. The difference in the peak shape is probably due to whether the cations are chemically formed or generated by the charge injection.

As indicated in Fig. 2, in the initial stage following voltage application, the SFG peaks originating from Alq_3 signal intensity in the initial stages of bias voltage application indicates that the negative charges at the Al cathode compensate for the negative polarization charges at the opposite Alq_3 interface. It should also be noted that following this decrease in Alq_3 SFG peak intensity, the intensities of the SFG peaks at 1497 and 1550 cm\(^{-1}\) increase. As previous FT-IR and Raman studies of potassium-doped Alq_3 indicated that the anionic state of Alq_3 exhibits signals at 1350, 1450, 1493, and 1550 cm\(^{-1}\),\(^{22}\) it appears that the peaks at 1497 and 1550 cm\(^{-1}\) are derived from the anionic Alq_3 species. In addition, the increased intensities of these signals indicate that Alq_3 anions are generated in the electron transport layer following compensation for the polarization charges, and that their quantity increases with increasing charge flow.

With respect to charge carrier transport and accumulation in the OLEDs, Fig. 4 shows schematic illustrations of the transient charge carrier behavior in the multilayer OLEDs in both the on and off states. In Fig. 4, we also show the time revolution of the SFG peak strengths of the α-NPD cations (1570 cm\(^{-1}\)), Alq_3 anions (1497 cm\(^{-1}\)), and the neutral Alq_3 (1387 cm\(^{-1}\)) deduced from the fitting of the SFG spectra in Fig. 2. Prior to the application of the pulse voltage, polarization charges exist at the Alq_3 interface and a potential gradient is formed inside the electron transport layer. Upon the initial application of a pulse voltage, electrons are transported to the Al electrode, and any apparent polarization charges in the Alq_3 layer are canceled by these negative charges. Subsequently, flat-band conditions are achieved throughout the device and the actual device current is obtained (region 1 of Fig. 4). At this point, α-NPD cations are formed at the α-NPD/HAT-CN interface (region 2 of Fig. 4), leading to an increase in the number of the positive charges within the α-NPD layer, and an increase in the SFG signal strength of the neutral α-NPD, thereby indicating charge accumulation at the α-NPD layer (region 3 of Fig. 4). This stage also involves the generation of Alq_3 anions through electron injection from the electrode adjacent to the Alq_3 layer. Since neither electrons nor holes have reached the light-emitting layer at this point, no light emission is observed. However, after 1 μs, emission from the OLEDs commences, thereby indicating that both electrons and holes have reached the emission layer (region 4 of Fig. 4).

Upon switching off the pulse voltage, light emission from the OLEDs begins to decrease in intensity as the injection of the charges stops. This is accompanied by the disappearance of the α-NPD cations and Alq_3 anions (region 5 of Fig. 4). In addition, owing to charge recombination at the α-NPD/HAT-CN interface, the number of the positive charges present at the α-NPD layer rapidly decrease. In the Alq_3 layer, the negative charges are first drawn back towards the Al electrode, resulting in an increase in the intensity of the SFG peak corresponding to Alq_3 due to the polarization charges of the Alq_3 layer (region 6 of Fig. 4). Although phosphorescent light emission from the emission layer continues beyond 1 μs after switching off the pulse voltage, charge transport is almost complete in the OLEDs, thereby resulting in the OLEDs returning to their original state where no charge is applied (region 7 of Fig. 4).

In conclusion, we herein reported the first application of time-resolved EFI-SFG spectroscopy under doubly resonant conditions for the investigation of the charge carrier behavior in a multilayer OLED device. Through the application of a
square wave pulse bias to the OLEDs, compensation for the polarization charges in the electron transport layer was clearly observed. In addition, after achieving flat-band conditions, the generation of $\alpha$-NPD cations and Alq3 anions was confirmed. Subsequently, upon switching off the pulse voltage, the $\alpha$-NPD cations disappeared immediately, indicating that charge recombination occurs at the interfaces. We therefore concluded that time-resolved EFI-SFG is a useful technique of probing the carrier behavior at the buried interfaces of organic devices as well as of identifying the origin of the charge carriers in OLEDs, which are essentially inaccessible by other techniques.

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