Degradation studies on high-voltage-driven organic light-emitting device using in situ on-operation method with scanning photoelectron microscopy

J. Lee,1 S. Sohn,1 H. J. Yun,2 and H. J. Shin3,8)
1Korea Basic Science Institute, Dukjin Dong 1-Ga 664-14, Jeonju 561-756, Republic of Korea
2Information Communication University, Daejon 561-756, Republic of Korea
3Pohang Accelerator Laboratory, POSTECH, Pohang 790-784, Republic of Korea

(Received 8 April 2008; accepted 15 September 2008; published online 3 October 2008)

We investigated the degradation behavior of a high-voltage-driven organic light-emitting device (OLED) by operating the device in an ultrahigh-vacuum environment. In situ on-operation method provided the initial degradation process when the OLED was biased inside an analysis chamber. The degraded area was probed by scanning photoelectron microscopy (SPEM) using synchrotron. SPEM showed that the degradation was accompanied by a local drift of indium tin oxide (anode) toward Al (cathode) and that the heat from the degraded area separated the cathode from the Alq3 layer, forming large bubbles. These results also indicate that microbubbles were formed under the Alq3, implying, before popping, the existence of local high-temperature degradation spots. © 2008 American Institute of Physics. [DOI: 10.1063/1.2994668]

Since organic light-emitting devices (OLEDs) first drew attention as a next-generation information display application, there have been many efforts to increase their device lifetime and efficiency.1–5 Even though lifetime and efficiency have become the most critical issues, a significant key factor, the OLED degradation process, remains only partially investigated.6–14 We recently reported a degradation study using scanning photoelectron microscopy (SPEM) with a biased external voltage; however, the mechanism of the degradation process inside OLEDs is as yet debatable.15 Probing the degradation of organic devices is extremely difficult because the multiple organic layers are sandwiched between thick electrodes. These metal electrodes have to be effectively removed without damaging the internal structures in order to obtain spectroscopic information, including visible chemical state information and electronic structure changes from the degraded area. Furthermore, polymers are usually sensitive to the incident electron beam and x ray, making analysis even more difficult. In addition, the surface of the degraded area should be secured from external contamination before being probed by analytical tools. A practical solution that adequately overcomes such issues is to reveal the degraded area by operating the device in a vacuum and to probe the chemical state information with a scanning photoelectron microscope. We have called this method “in situ on-operation analysis (ISOA).” In the present study, we performed ISOA to investigate the degradation mechanism on a bottom-emission OLED. The ISOA with SPEM was demonstrated to be an effective analytical technique to study the OLED degradation process, specifically by eliminating external factors such as water, gases, and others, thereby retarding the degradation speed. Thus, we were able to observe the degradation process in which the indium tin oxide (ITO) drifts toward the Al electrode at the edges of the exploded area, those hot gases from the edges causing segregation between the Al electrode and the Alq3 layer, forming a large bubble that eventually popped.

This study was carried out by means of SPEM using a Fresnel zone plate16 at the 8A1 beam line at Pohang Light Source. The structure of the OLED used for the analysis is as follows: a passivation cap, Al electrode (150 nm), LiF (0.7 nm) interlayer, electron transport layer (ETL) (Alq3; 25 nm), emissive layer (EML) (Alq3+C545T:35 nm), hole transport layer (HTL) (NPB, 20 nm), hole injection layer (HIL) (NPB, 60 nm), ITO (80 nm), SiN (300 nm), and glass as a substrate (in order). The passivation cap was removed before mounting the sample onto a preparation chamber, in which the base pressure was 4 × 10−10 Torr. The sample was externally biased to operate the device inside the UHV chamber, as shown in Fig. 1(a). The bias voltage was intentionally increased until the initial degradation process began. At 20 V, a large bubble formed in the central part of the device and eventually, after 10 s, popped, revealing the degraded area shown in Fig. 1(b). Most of the other bubbles, excepting the large one at the center, remained. The exposed area was then probed by SPEM. The x ray was incident normal to the sample surface and the energy of the x ray was 630 eV. The analyzer collected photoelectrons with the analyzer axis 55° off surface normal (the ideal geometry for topologically enhanced SPEM images). The spectral energy resolution of the SPEM is 0.3 eV. The spatial resolution is 0.5–1.0 μm. The binding energy of each spectrum was calibrated using the Al 2p spectrum from Al metal.

FIG. 1. (Color online) (a) Photo of OLED under in situ on-operation in vacuum. (b) Photo of degraded OLED after applying 20 V bias for 10 s.
Figure 2 shows SPEM images of (a) the In 3d, (b) the O 1s, (c) the sample current, (d) the C 1s at 285.8 eV, (e) the C 1s at 285 eV, and (f) the C 1s at 284.2 eV of the popped-bubble region, as indicated in Figs. 2 and 4. Only the edge of the popped-bubble region shows distinguishable contrast/spectral features as shown in the sample current image (g) [enlarged image of the box in Fig. 2(e)]. Since the electron escape depth of primary photoelectrons is less than a few nanometers, the appearance of the In 3d and the O 1s in the central part of the popped-bubble area showing topology-enhanced microbubbles.

The spectra obtained in the central part of the popped-bubble area showing topology-enhanced microbubbles.

FIG. 2. (Color online) SPEM images (60 × 60 pixels) including the popped region of the dotted box (60 × 60 μm²) in Fig. 1(b). (a) In 3d, (b) O 1s, (c) sample current (Ref. 17), (d) C 1s at 285.8 eV, (e) C 1s at 285 eV, and (f) C 1s at 284.2 eV images are shown. (g) is a sample current image showing details at the edge of the popped-bubble area. (h) and (i) are the C 1s images obtained in the central part of the popped-bubble area showing topology-enhanced microbubbles.

FIG. 3. (Color online) (a) Survey spectra obtained from the central [“1” (outside) and “2” (on the microbubble)] and edge (“3”) regions of the popped-bubble area, as marked in Figs. 2(g) and 2(i). (b) The spectra obtained after sputtering on marks A (central region) and B (edge region).

FIG. 4. (Color online) High-resolution spectra obtained for (a) C 1s, (b) N 1s, and (c) In 3d spectral components obtained from the central (1 and 2) and edge (3) regions, as indicated in Figs. 2(g) and 2(i).
the spectra (Figs. 3 and 4) obtained at the edge indicates that
the ITO drifts to the surface, presumably through the Alq3
layer, and that the polymer layer on the ITO becomes thin
due to the polymer-layer ablation resulting from the heat in
this region. The sample current was stronger owing to the
stronger absorption coefficient of the ITO compared with
that of the polymer. In the central popped-bubble area, since
the C 1s was the main component having a weak N 1s peak
(Fig. 3(a), 1 and 2), the Al cathode structures including the
LiF interlayer were blown away because the bonding be-
tween the Al layer and the organic layer in the given geom-
etry is the weakest.

One noticeable thing is the observation of microbubbles
[topology-enhanced images (h) and (i)]. The spectral features
of both on and outside the bubbles are the same, as shown in
Fig. 3(a) (1 and 2). Indeed as shown in the high-resolution x-ray
photoemission spectroscopy spectra (1 and 2 in Fig. 4), the
chemical states of C 1s and N 1s are the same in the
images, the contrast having been produced by the topology
effect. Considering the angle between the surface normal and
the analyzer axis (55°), the estimated height of the micron-
size bubbles is of the order of 1 μm and the size of a few
micrometers. The gas formation induced by the local heat
eventually gave rise to the microbubbles under the Alq3 layer
at the shallowest point.

As shown in Fig. 4, the InO (main peak) and the metallic
In (small peak), with the formation of the different chemical
states of nitrogen and carbon (the N 1s and C 1s peaks in
Figs. 3 and 4), suggest that the temperature was high enough
to decompose the polymer layers in the edge region, where
the ITO appeared to be drifted toward the electrodes. Such
evaporated/decomposed polymer produces hot gases, eventu-
ally causing large bubbles to form. The polymers, which pre-
vented thickness is a few tens of nanometers. In the central
popped-bubble region, we were able to observe many micro-
bubbles that resulted from the local high-temperature heating.
The in situ on-operation method with the SPEM

technique enabled us to observe the part of the initial stage of
the degradation process. Study on the initial degradation of

In summary, the ITO drift through the electron path in-
duces the high-temperature local heat, producing hot CNx
gases. These gases give rise to the gradual segregation of the
electrodes from the organic layer with the formation of large
bubbles that subsequently pop. Beneath the Alq3 layer in the
popped-bubble region, we were able to observe many micro-
bubbles from the organic layer with the formation of large
bubbles that subsequently pop. Beneath the Alq3 layer in the
popped-bubble region, we were able to observe many micro-
bubbles that resulted from the local high-temperature heating.

This work was supported mainly by a KBSI research
grant (Grant No. N28038).

(2007).
Lett. 82, 173 (2003).
11, 605 (1999).
6L. Ke, S. J. Chua, K. Zhang, and N. Yakovlev, Appl. Phys. Lett. 80, 2195
(2002).
7M. Y. Chan, S. L. Lai, F. L. Wong, O. Lenguel, C. S. Lee, and S. T. Lee,
8R. Czew, D. C. Carroll, H. S. Woo, Y. B. Kim, and J. W. Park, J. Appl.
10M. Fujihira, L. M. Do, A. Kiske, and E. M. Han, Appl. Phys. Lett. 68,
1787 (1996).
14P. Melpignano, A. Baron-Tolado, V. Biondo, S. Priante, R. Zamboni, M.
Murgia, S. Caria, L. Gregoratti, A. Barinov, and M. Kiskinova, Appl.
17The sample current was obtained by measuring the current flow (to
compensate the photoelectrons) from the ground to the sample. The sample
current image represents the distribution of changes in absorbance and the
electron yield of the photoelectrons.